Cathodic arcs and high power pulsed magnetron sputtering:

A comparison of plasma formation and thin film deposition

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Motivation: Film Formation by Energetic Condensation

- Energetic Condensation:
  - Growth of films from hyper-thermal species
  - Kinetic energy > Surface and bulk displacement energy
  - Subplantation

- Film properties:
  - good adhesion, intermixed layer
  - dense
  - often with enhanced hardness, Young's modulus
  - conformal coating of nanostructures, trench filling possible
  - usually under intrinsic compressive stress

Motivation: Film Formation by Energetic Condensation

- High kinetic energy of film-forming species obtained via ***plasma*** in combination with ***bias***

Ion Energy

Implantation

Film growth is still possible for low duty cycle of bias

sputter yield = 1 for E_i=300-1200 eV

Subplantation

Deposition

Ion plating, MePIIID

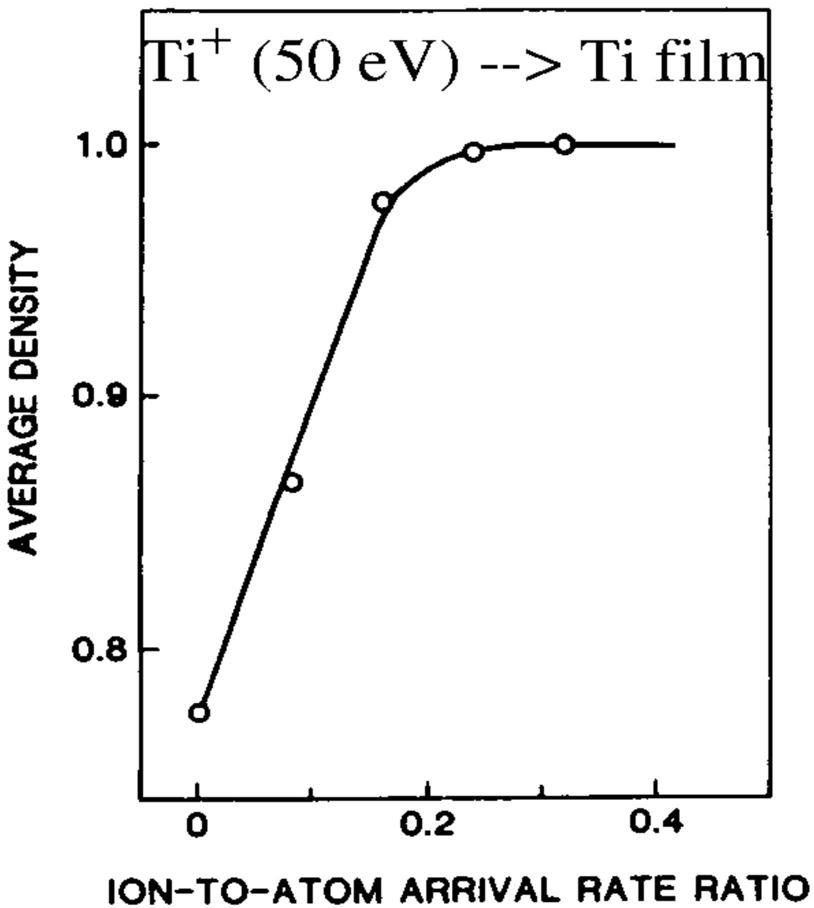
cathodic arc deposition

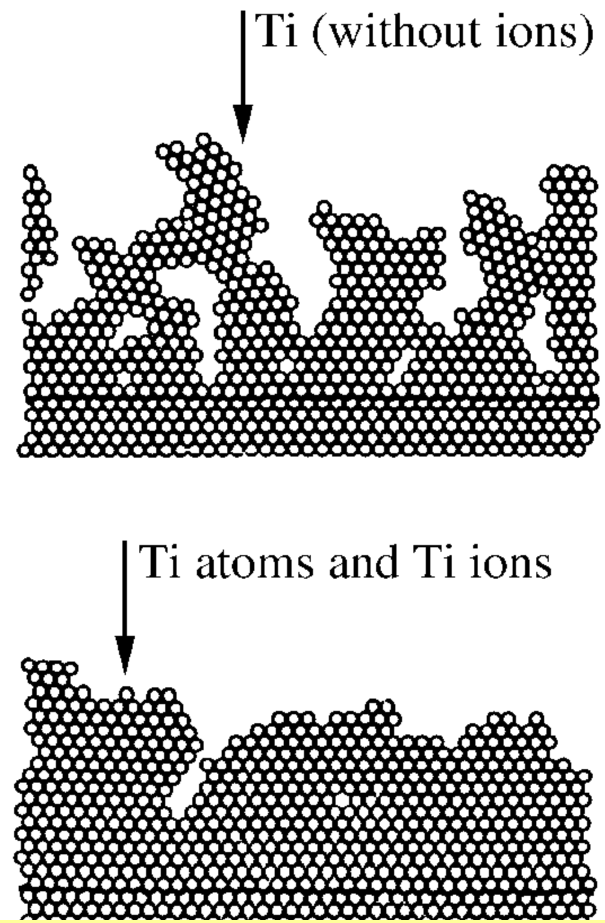
sputtering

evaporation

Effect of Self-ion Bombardment on Film Microstructure

- Densification of Ti film by Ti ions (self-ion assistance) at room temperature





Martin et al. *JVST* **5** (1987) 22

Cathodic Arc and Sputtering: A First Simplistic Comparison

	Cathodic Arc	Sputtering
source	cathode	target
background	vacuum or gas	gas
kinetic energy	high (> 20 eV)	low (<10 eV)
degree of ionization	very high	very low
mean ion charge state	usually 2^+	usually 1^+
macroparticles	yes	no

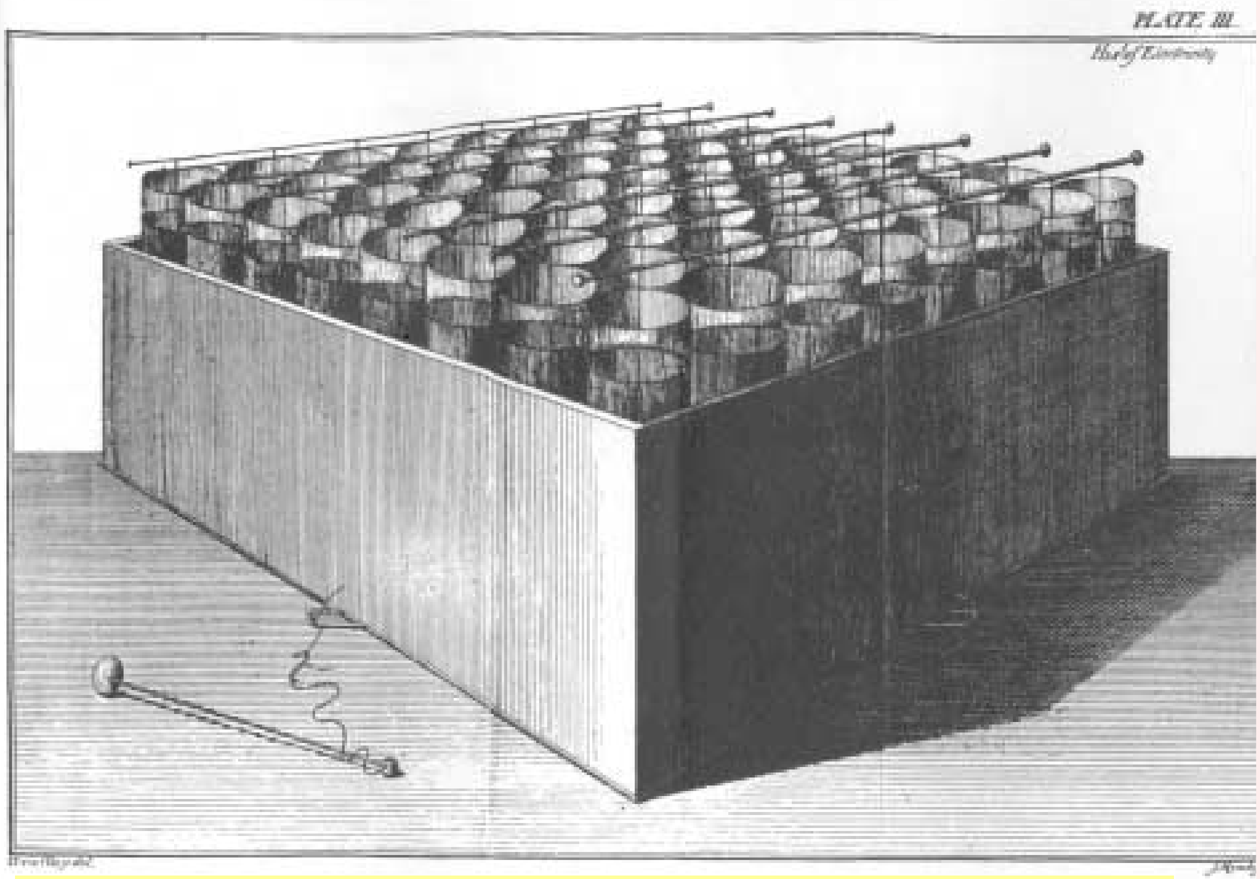
Filtered Arc and *Pulsed* Sputtering: A First Simplistic Comparison

	Filtered Cathodic Arc	*Pulsed* Sputtering
source	cathode	target
background	vacuum or gas	gas, ***sputtered material***
kinetic energy	high (> 20 eV)	low (<10 eV)
degree of ionization	very high	low - ***high***
mean ion charge state	usually 2^+	usually 1^+, *also* 2^+
macroparticles	very few	***few (arcing)***

Status Part 1: Cathodic Arc Plasmas

Cathodic Arcs: Oldest, still "Emerging" Plasma Coating

- Discharges and Plasmas were made as soon as energy storage was invented.



A. Anders, *IEEE Trans. Plasma Sci.* **31** (2003) 1052

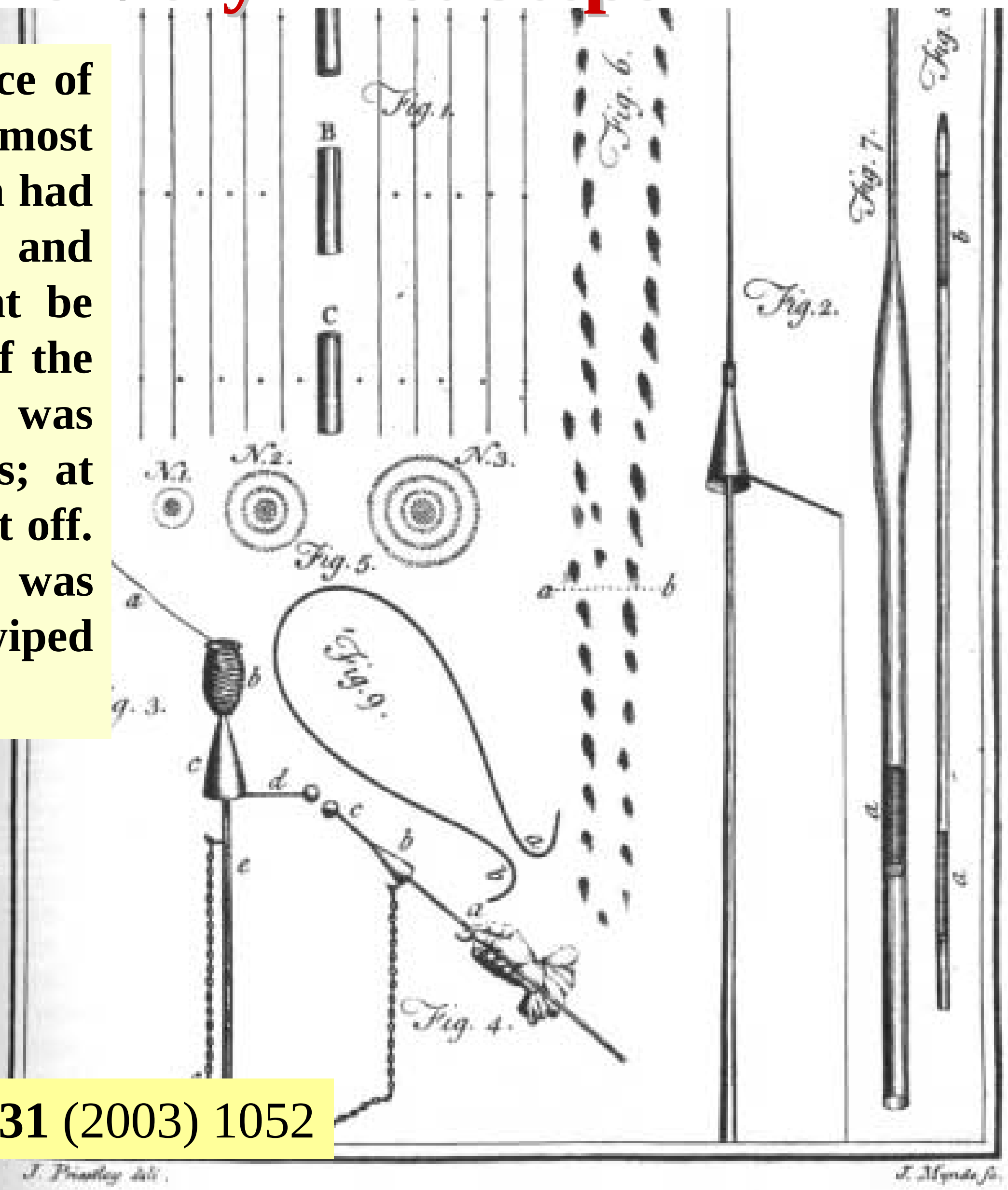
QUOTE Joseph Priestley:

"June the 13th, 1766. After discharging a battery, of about forty square feet, with a smooth brass knob, I accidentally observed upon it a pretty large circular spot, the center of which seemed to be superficially melted…

…Examining the spots with a microscope, both the shining dots that formed the central spot, and those which formed the external circle, appeared evidently to consist of cavities, resembling those on the moon, as they appear through a telescope, the edges projecting shadows into them, when they were held in the sun."

Cathodic Arc Plasma Coating on Glass: The Very First Steps

“I next laid the chain upon a piece of glass;…the glass was marked in the most beautiful manner, wherever the chain had touched it; every spot the width and colour of the link. The metal might be scraped off the glass at the outside of the marks; but in the middle part it was forced within the pores of the glass; at least nothing I could do would force it off. On the outside of the metallic tinge was the black dust, which was easily wiped off.” **Joseph Priestley, 1766.**



- Cathode spots
- Macroparticles
- Reactive deposition
- Coatings with good adhesion

A. Anders, *IEEE Trans. Plasma Sci.* **31** (2003) 1052

Cathodic Arcs: Explosive Plasma Formation at Cathode Spots

- plasma at cathode spots is formed explosively
- spot models include "explosive electron emission" and "ectons" (Mesyats)
- spot may have explosive and evaporative phases
- current density in explosive phase is high, ~ 10^{12} A/m^2
- voltage between electrodes is low, ~ 20 Volts, though areal power density is high, ~ 10^{13} W/m^2

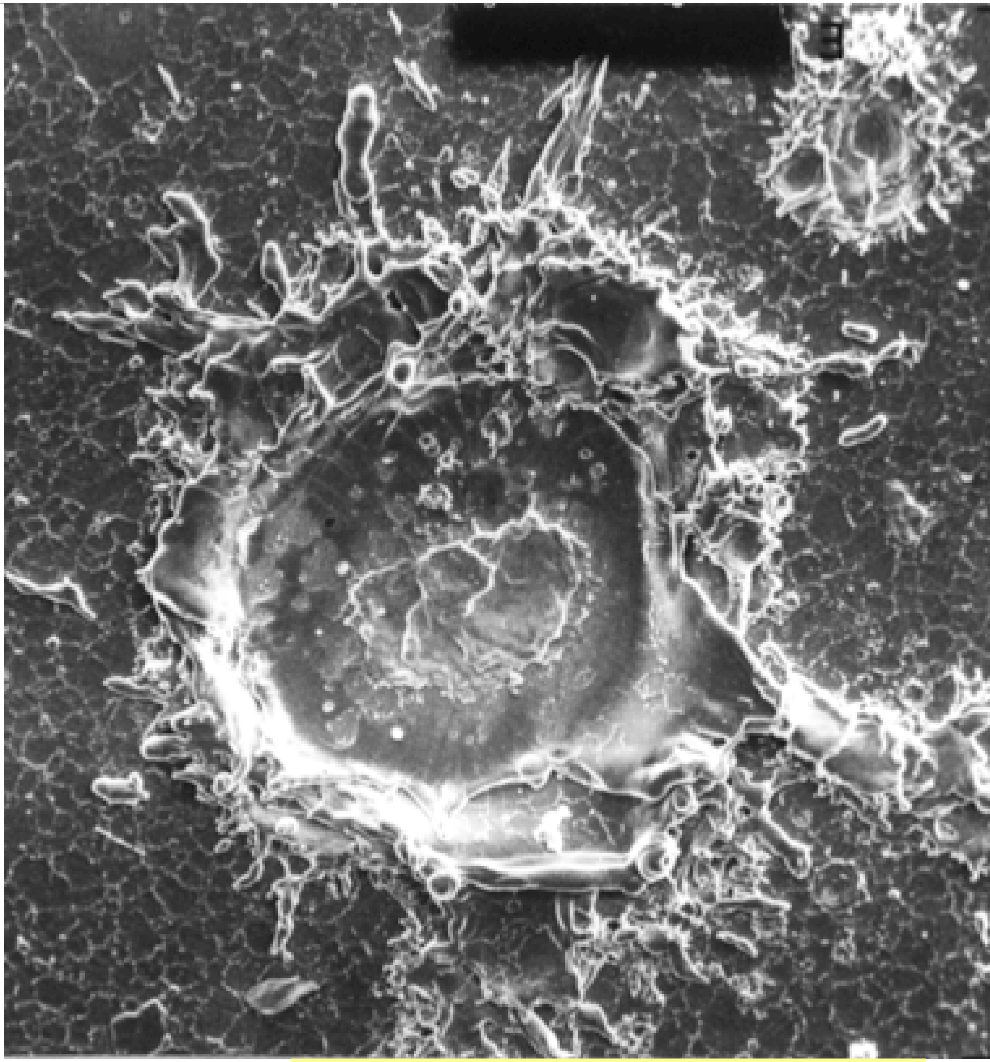
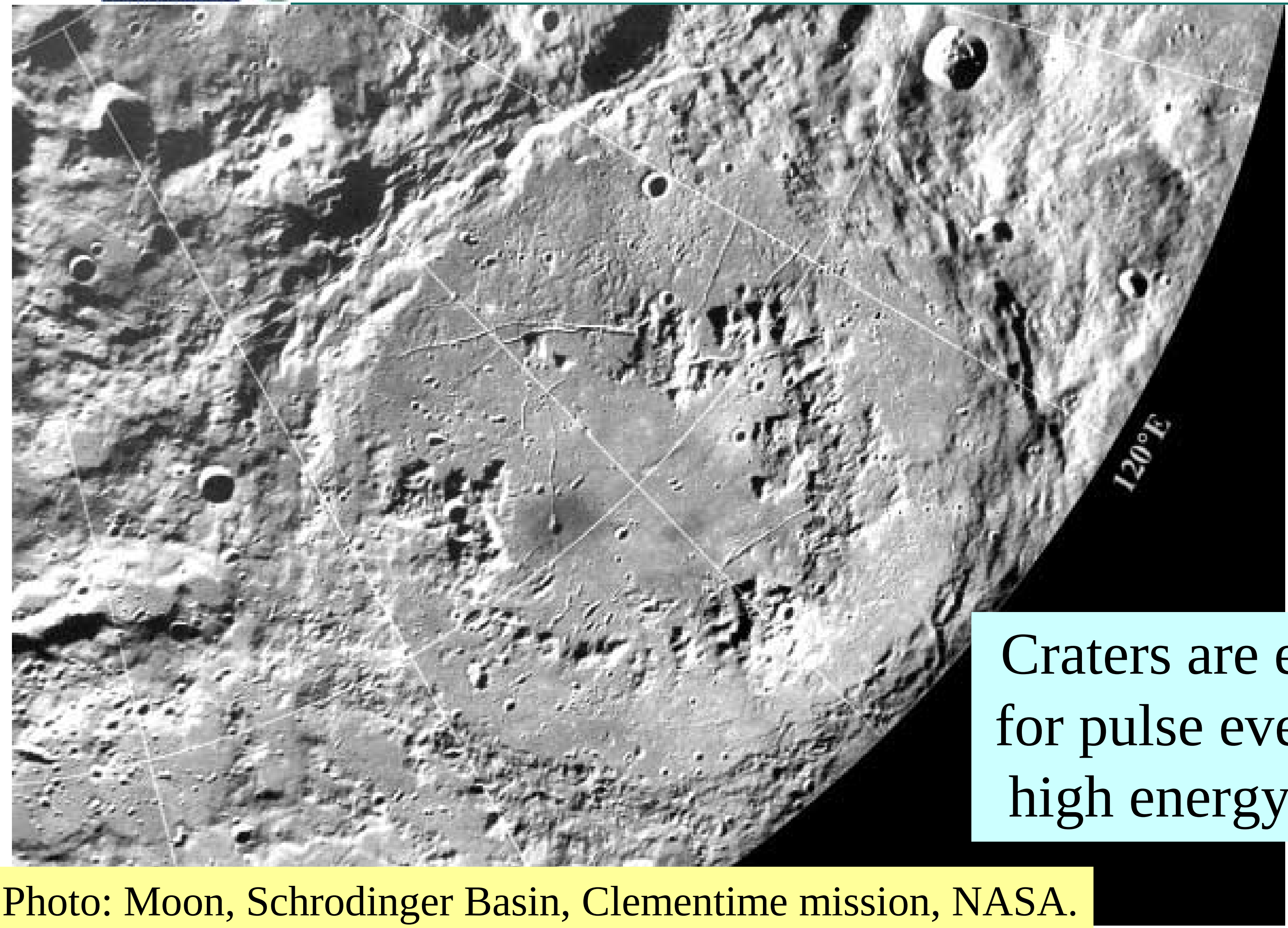


Photo courtesy of B. Jüttner

Events with High Energy Density

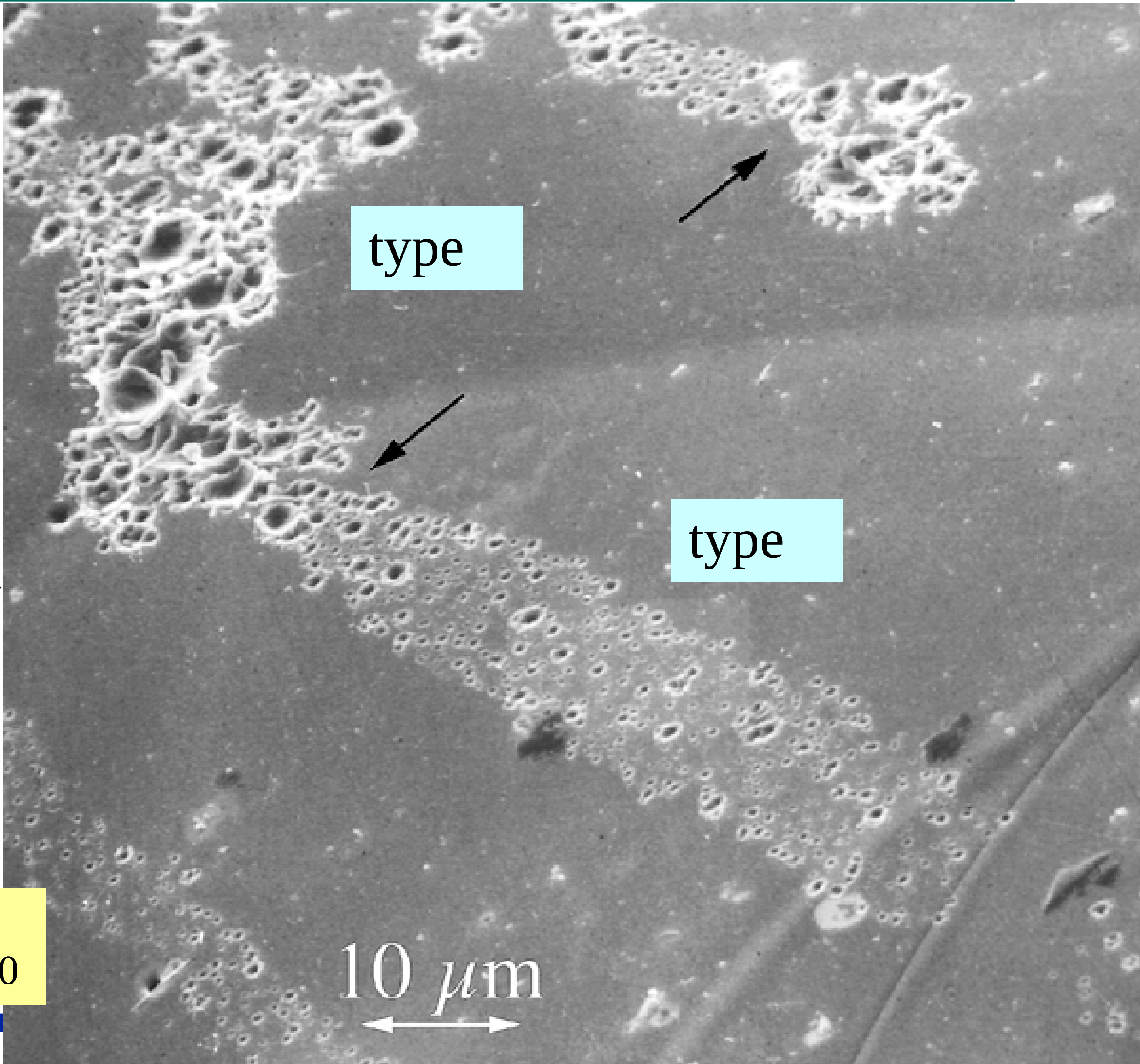


Craters are evidence for pulse events with high energy density

Photo: Moon, Schrodinger Basin, Clementime mission, NASA.

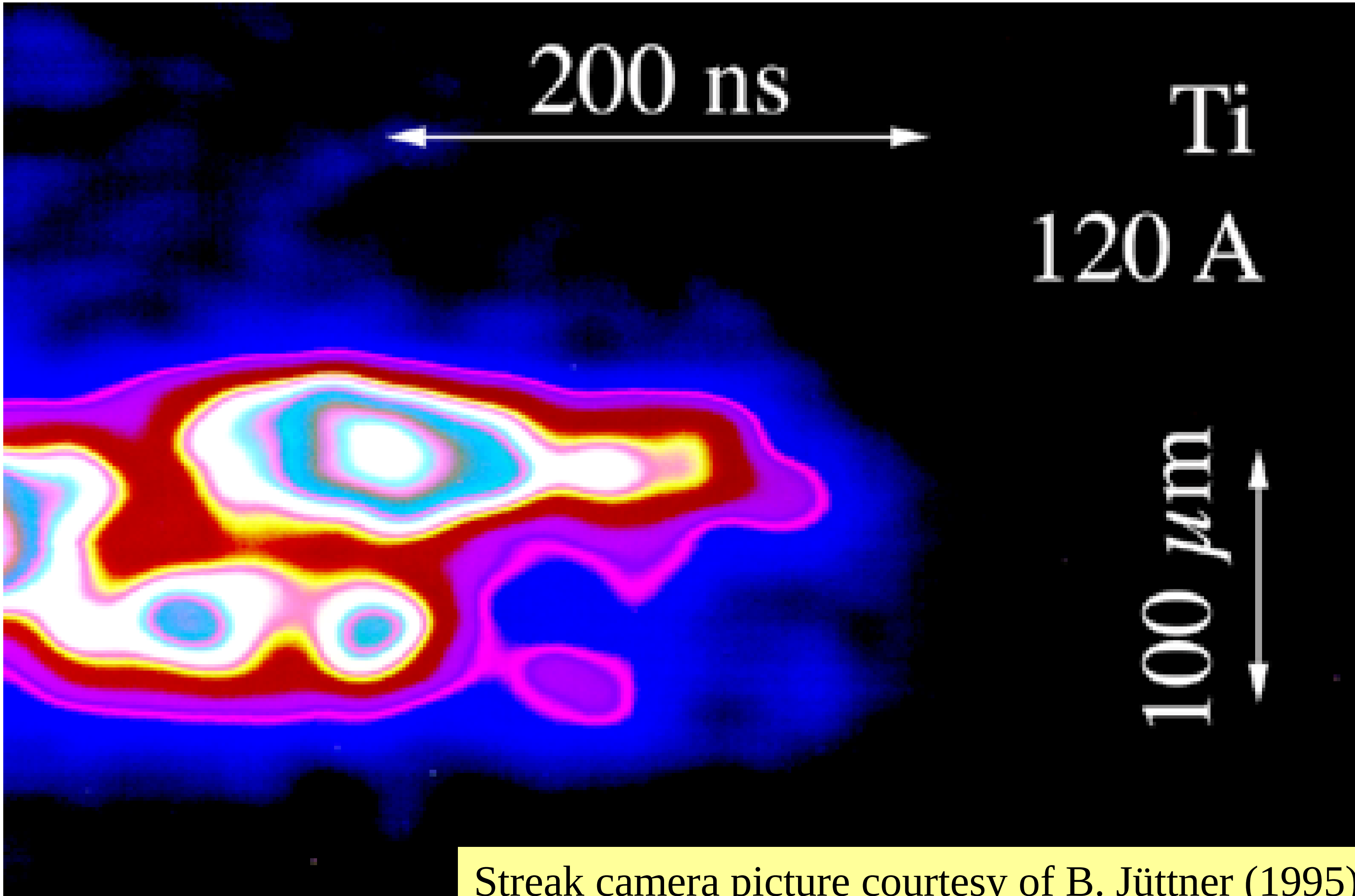
Explosive Cathode Erosion and Plasma Formation

- arc spots / spot fragments leave crater traces
- type or mode depends on surface condition



from A. E. Guile, B. Jüttner, ZIE Preprint 80-2, Berlin, 1980

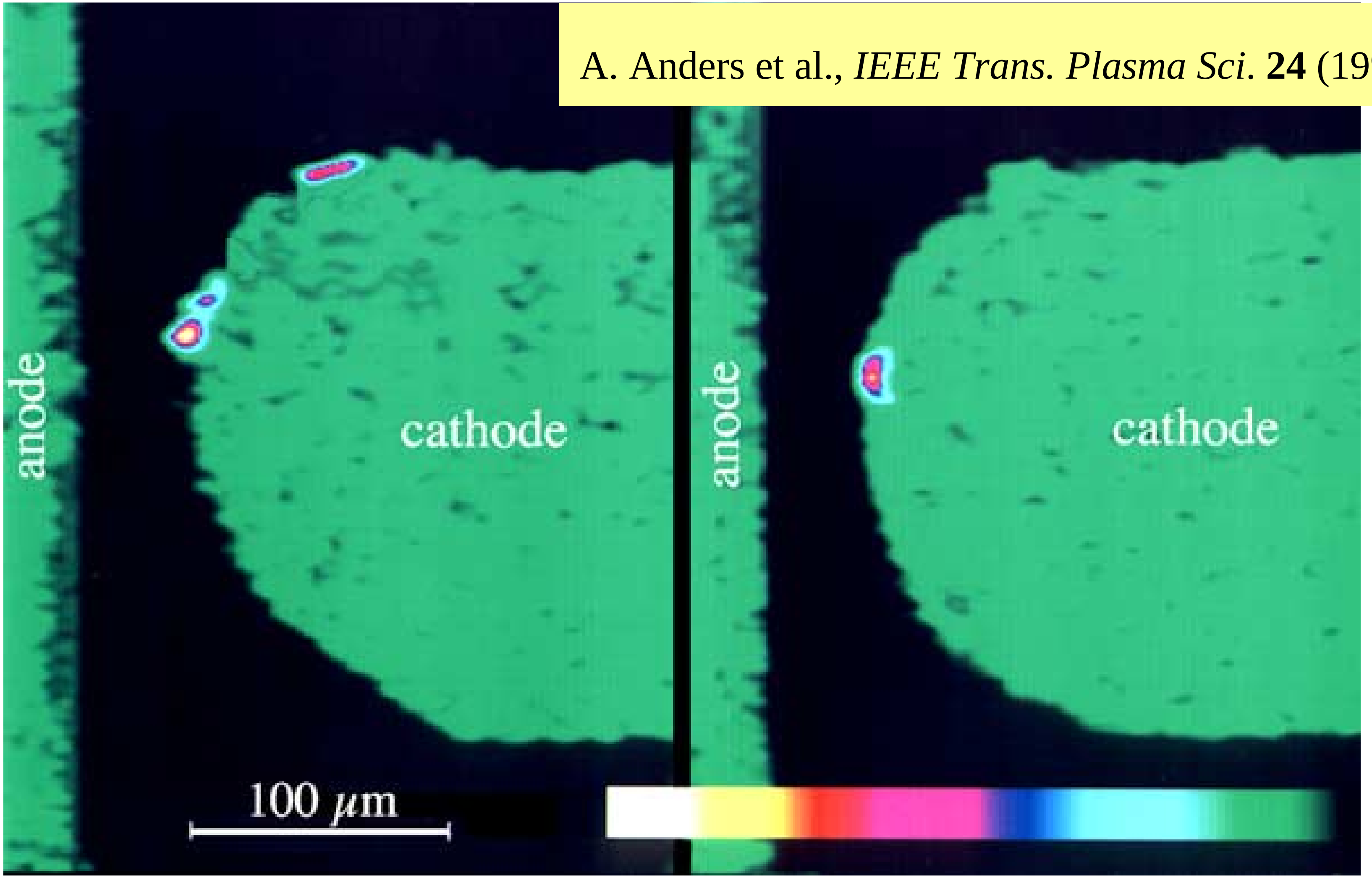
Dynamics of Arc Spots: High-Speed Photography



Streak camera picture courtesy of B. Jüttner (1995)

Dynamics of Arc Spots: Laser Absorption Photography

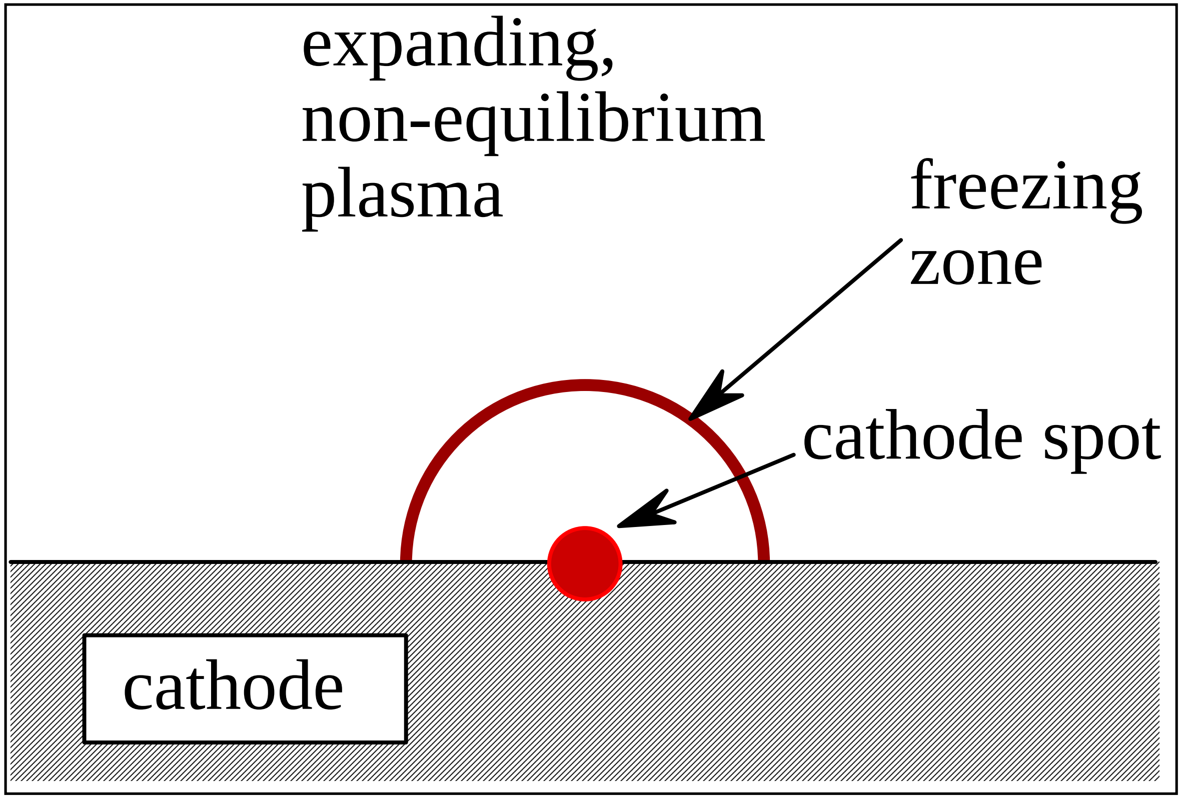
- development of cathode spots, Cu, 100 A, Δt between pictures 3ns



A. Anders et al., *IEEE Trans. Plasma Sci.* **24** (1996) 69

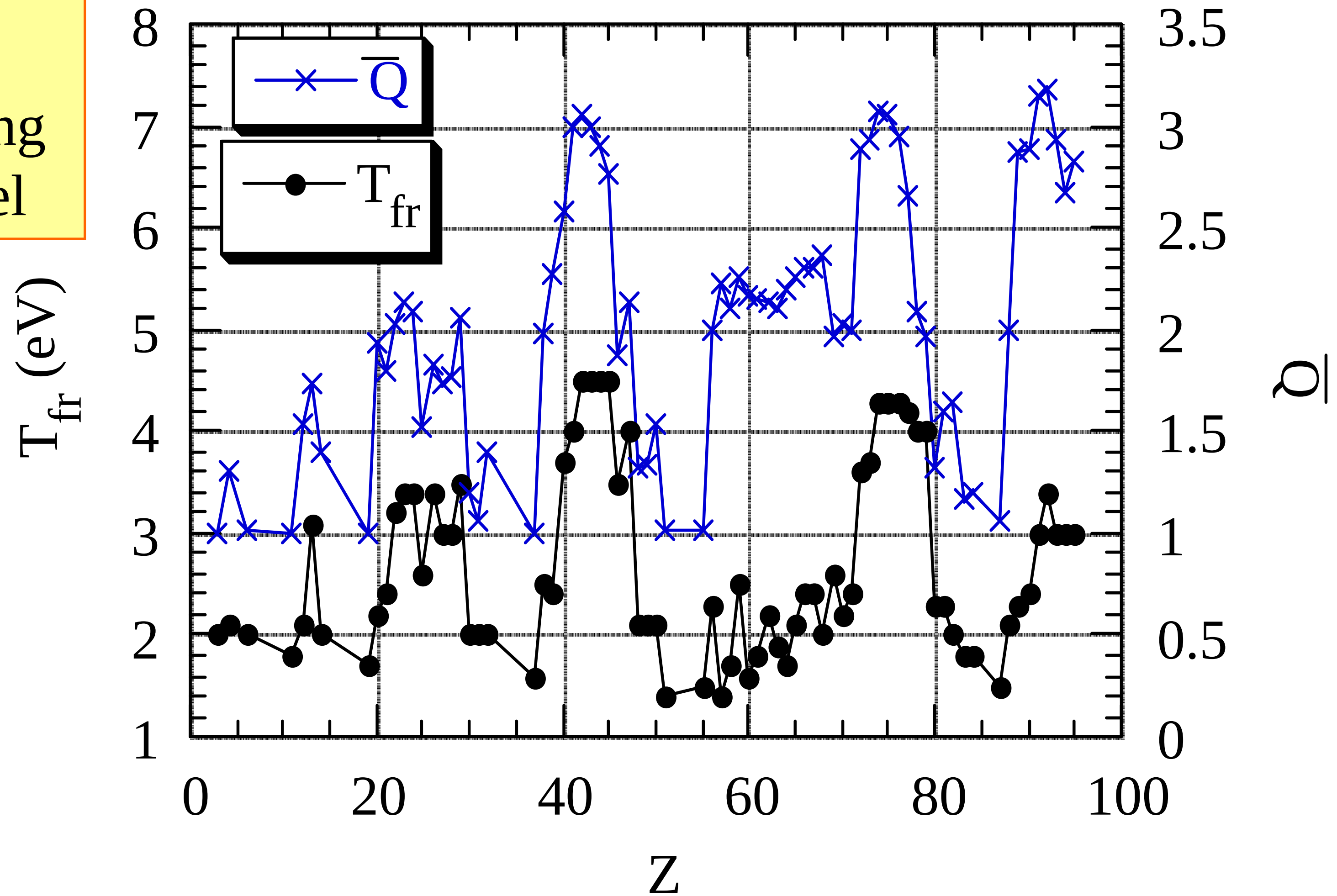
Cathode Spot Models

- Ion charge state spectrometry reflects plasma condition at equilibrium ⇒ non-equilibrium transition zone, the "freezing zone" near cathode spot



Ion Charge States and Electron Temperature

electron temperature derived by using freezing model



A. Anders, *Phys. Rev. E* **55** (1997) 969

Improved Freezing Model: *Partial Local Saha Equilibrium*

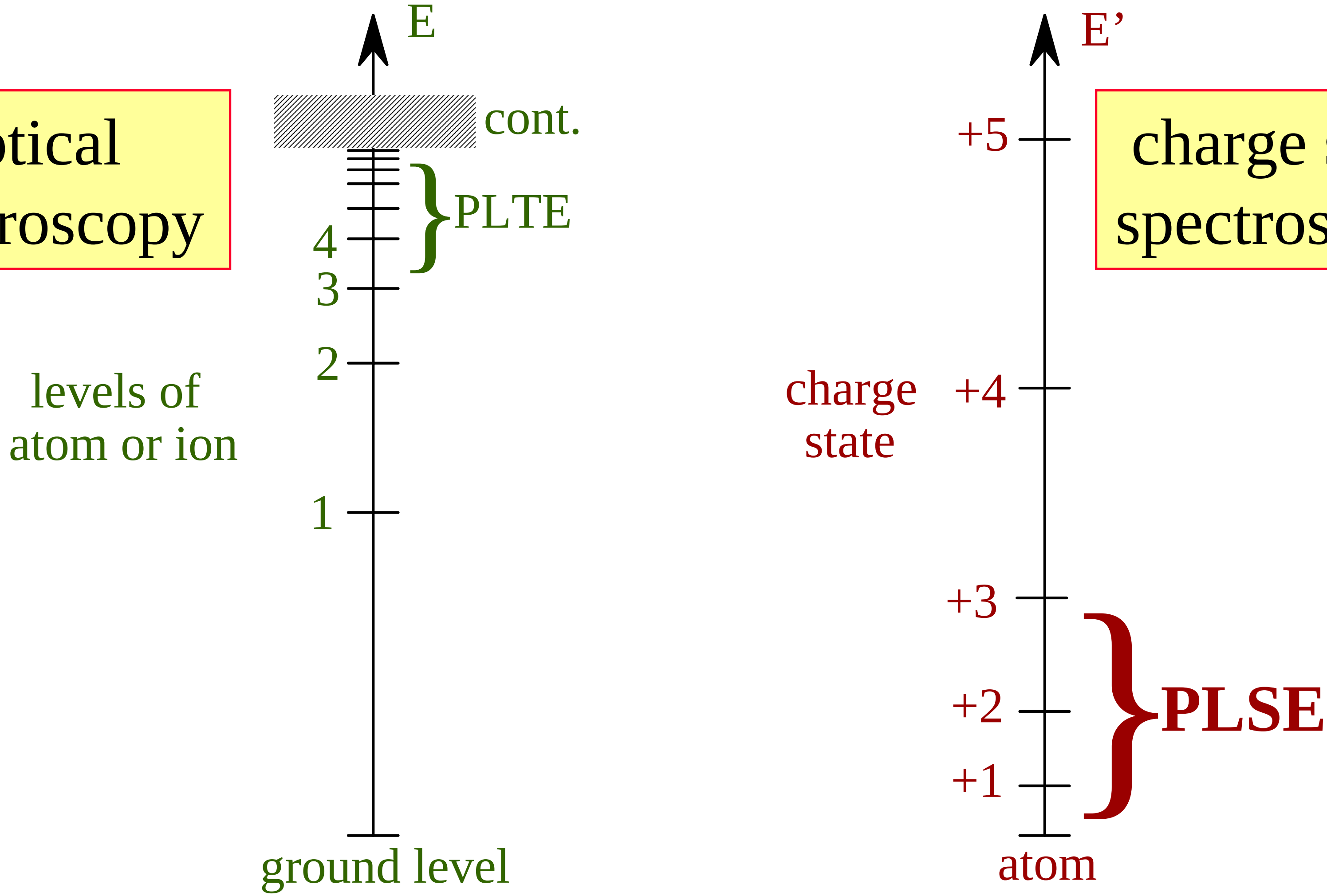
- Develop analogy to what is known in optical spectroscopy:
  - "Complete Local Thermodynamic Equilibrium" (CLTE)
  - "Partial Local Thermodynamic Equilibrium" (PLTE)
- Plasma *Optical* Spectroscopy:
  - system of excitation and de-excitation rate equations
- Plasma *Charge-State* Spectrometry:
  - system of ionization and recombination rate equations

$$\frac{\partial n_Q}{\partial t} = n_{Q+1} n_e^2 \alpha_{Q+1,Q} - n_Q n_e \beta_{Q,Q+1} \qquad \text{for } Q = 0$$

$$\frac{\partial n_Q}{\partial t} = n_{Q-1} n_e \beta_{Q-1,Q} + n_{Q+1} n_e^2 \alpha_{Q+1,Q} - n_Q n_e \beta_{Q,Q+1} - n_Q n_e^2 \alpha_{Q,Q-1} \qquad \text{for } Q > 0$$

Partial Local Saha Equilibrium

optical spectroscopy



charge state spectroscopy

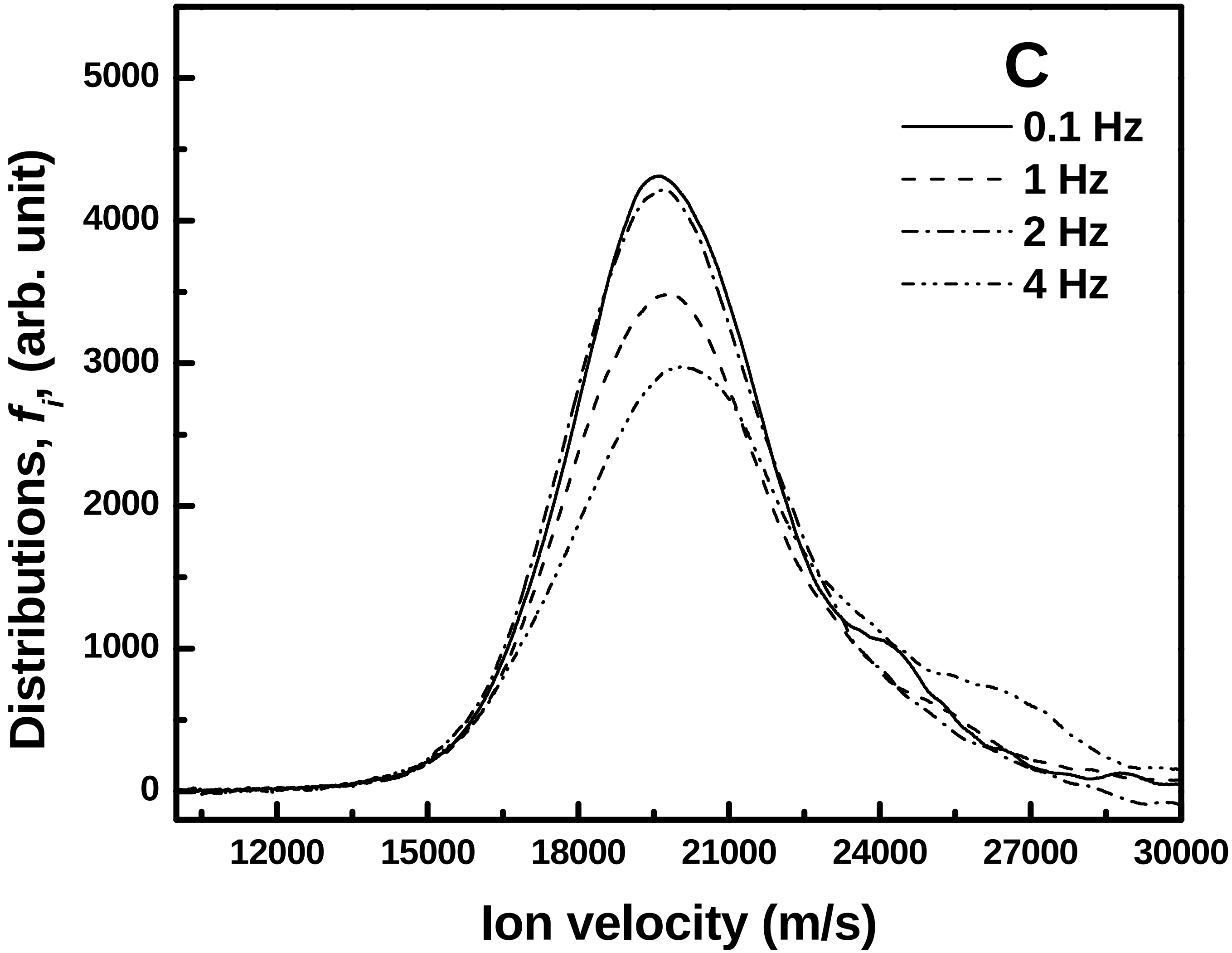
A. Anders, *IEEE Trans. Plasma Sci.* **27** (1999) 1060

Ion Acceleration at Cathode Spots

- Acceleration by
  - pressure gradients (e.g. multi-fluid theory)
  - electron-ion “friction”
- Ion drift velocity > Ion sound velocity, **M**=3-6
- Ion drift velocity almost independent of charge state
- may consider plasma jet as a fully-compensated, low-energy ion beam, 20-150 eV

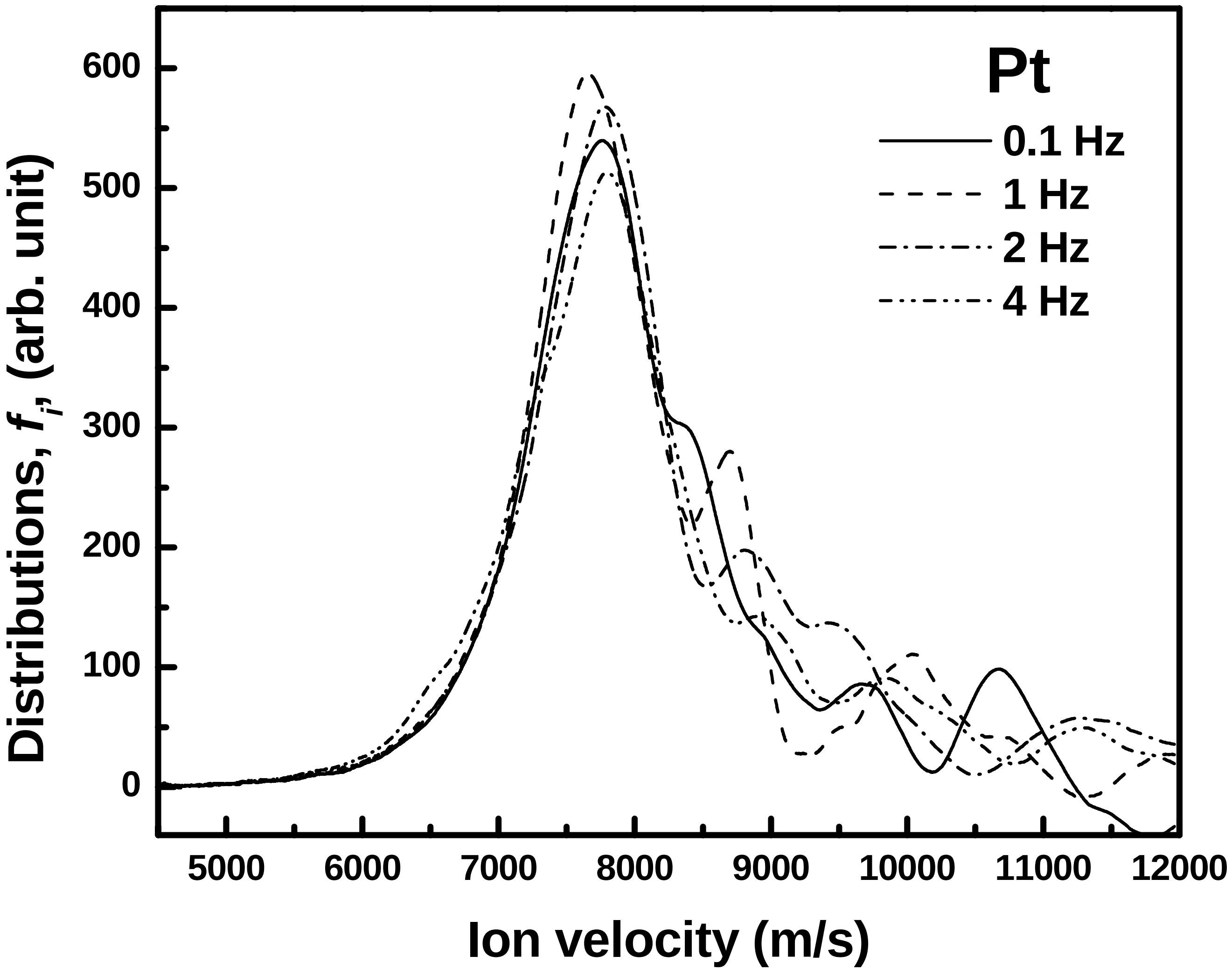
most complete table of experimental velocity data:
Anders and Yushkov, *J. Appl. Phys.* **91** (2002) 4824

Example: Carbon Vacuum Arc Ion Velocity Distribution Function



E. Byon and A. Anders, *J. Appl. Phys.* **93** (2003) 1899

Example: Platinum Vacuum Arc Ion Velocity Distribution Function



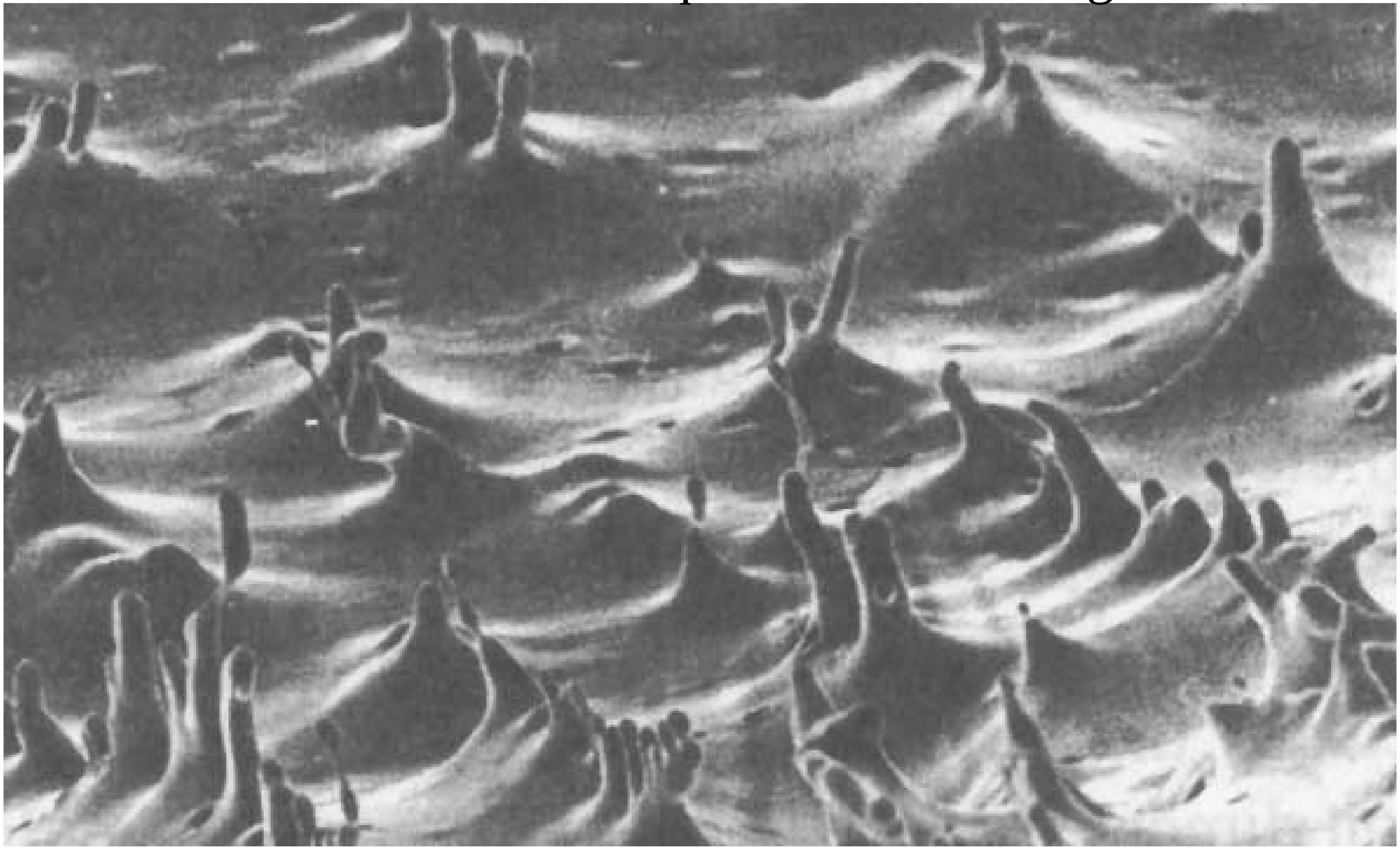
E. Byon and A. Anders, *J. Appl. Phys.* **93** (2003) 1899

Macroparticles

- Ion bombardment of the cathode can melt the surface layer
- the melted surface is subject to the momentary, “pulsed” ion pressure
- video clip: response of liquid surface to pulsed pressure

Explosive Emission and Macroparticle Formation

"Frozen" nonlinear wave of liquid metal in strong electric field



Gabovich and Poritskii, *JETF Lett.* **33** (1981) 304

Macroparticle Formation

- Macroparticles are formed as part of the explosive plasma formation
- Typical: Material is ejected from the liquid pool between plasma and solid

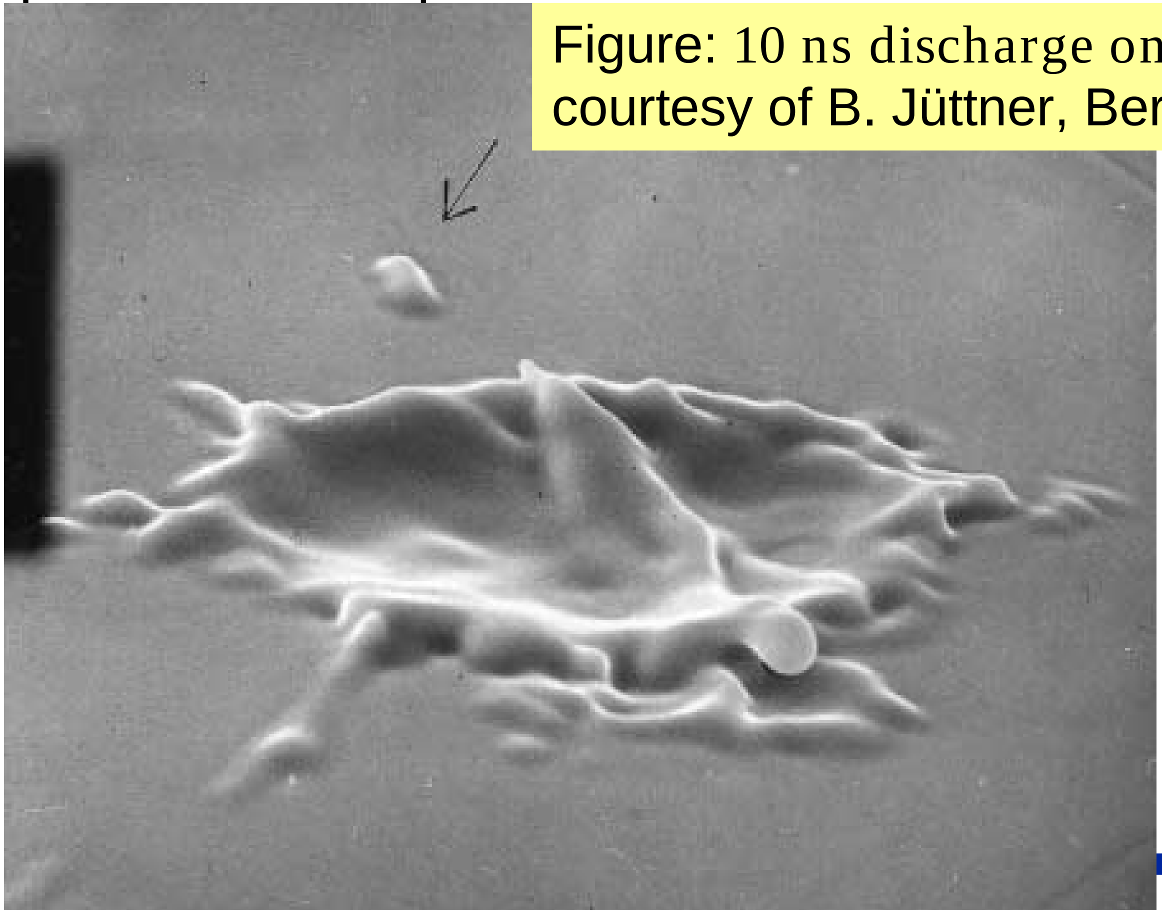
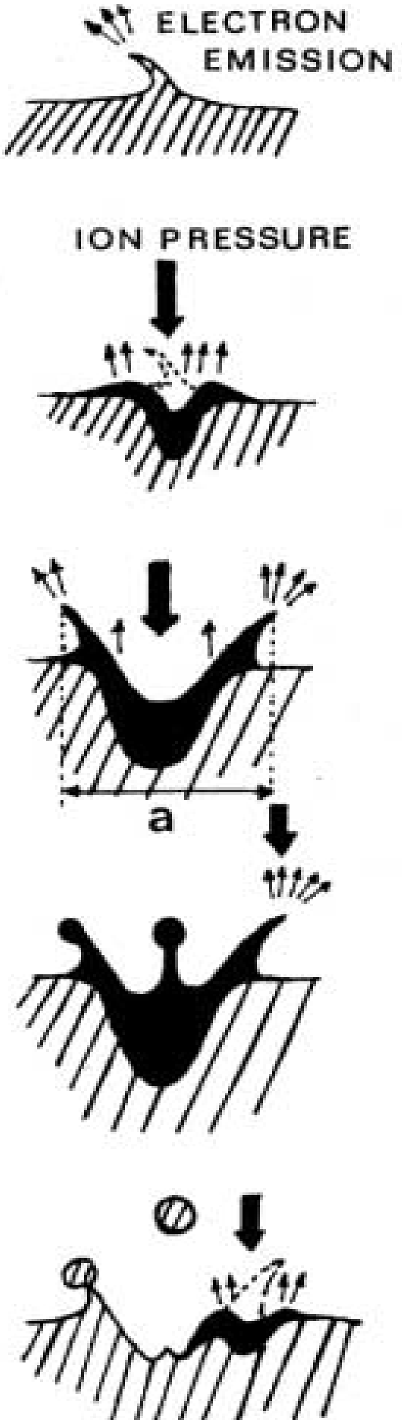
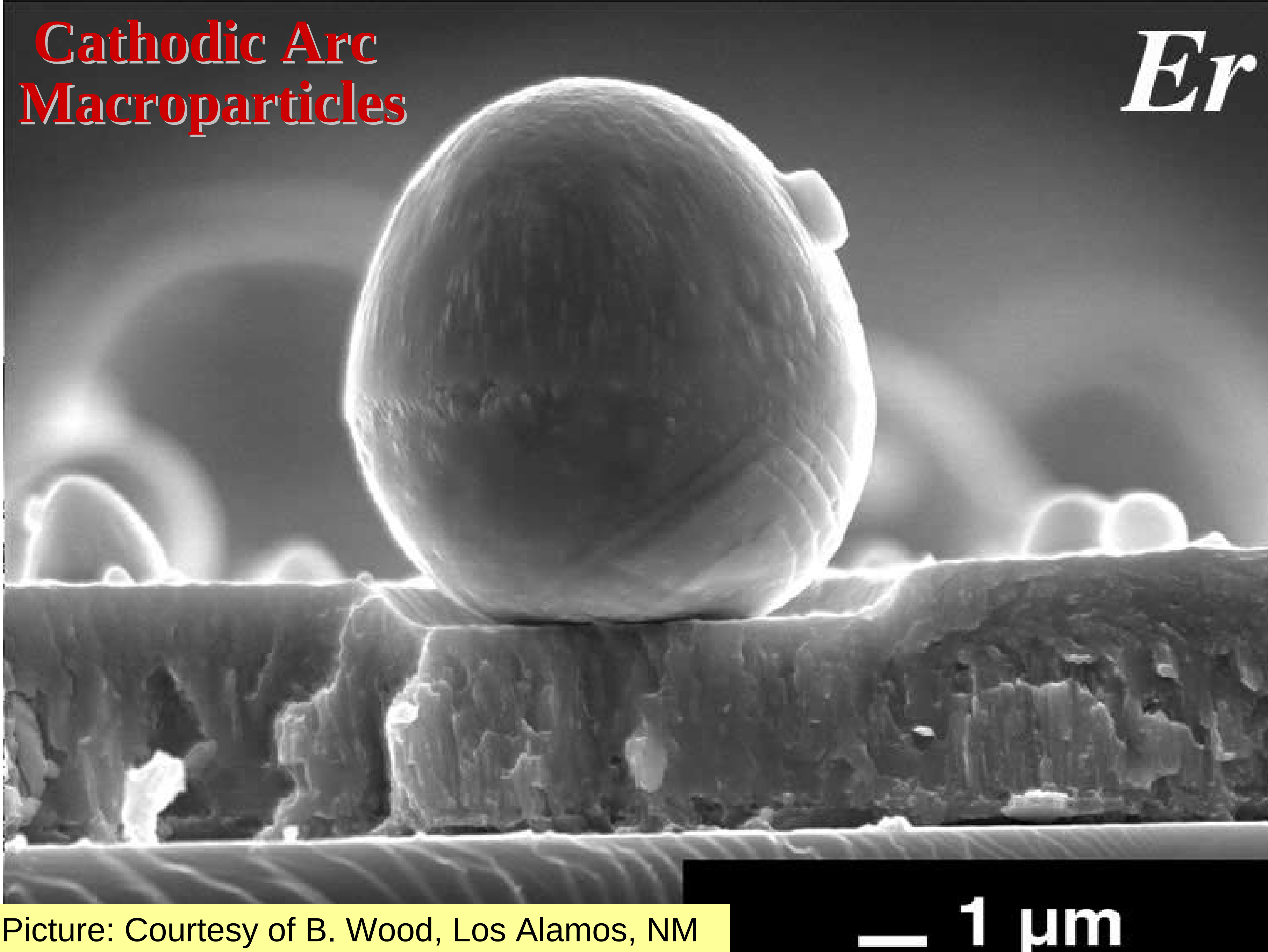


Figure: 10 ns discharge on Mo courtesy of B. Jüttner, Berlin



Cathodic Arc Macroparticles



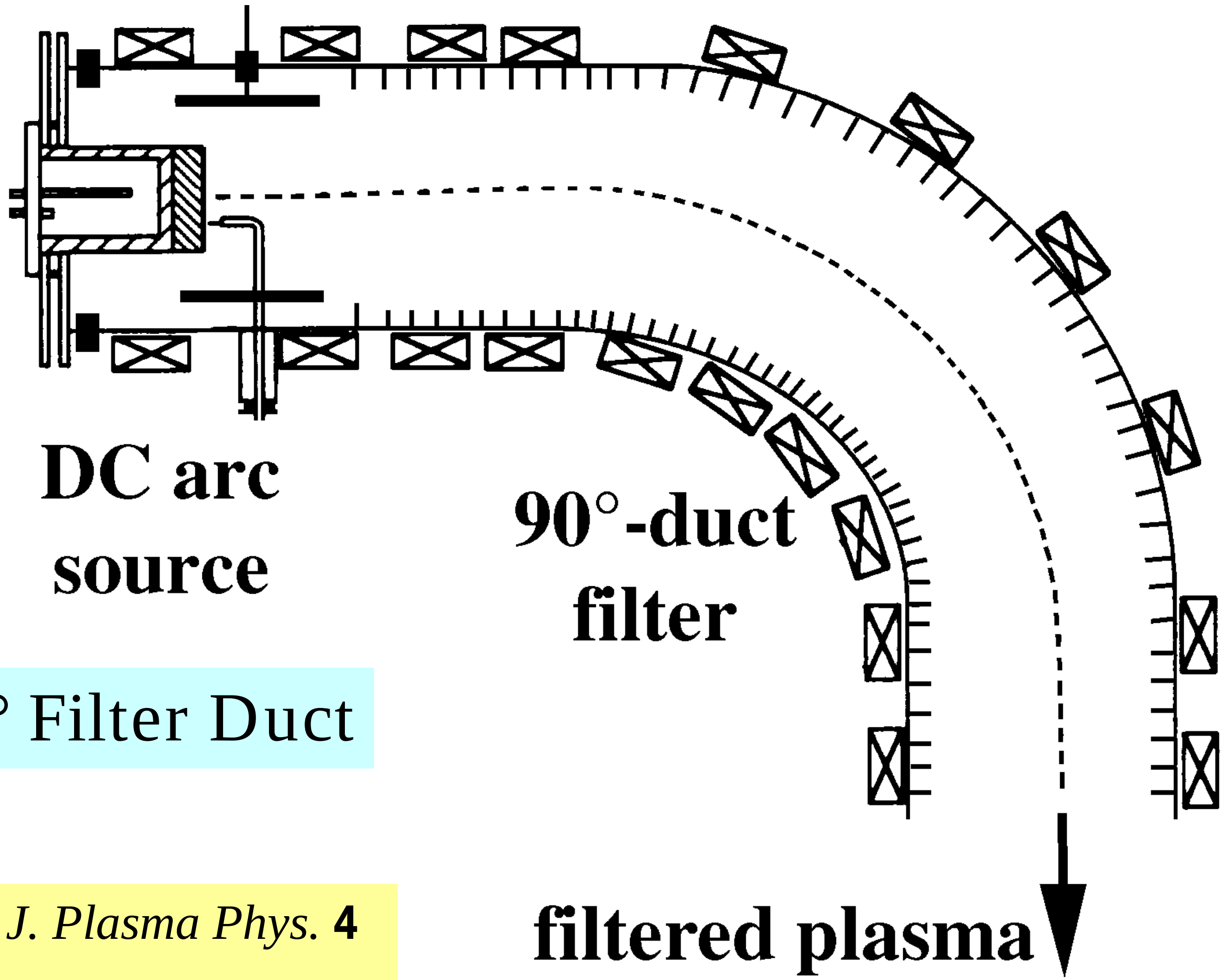
Picture: Courtesy of B. Wood, Los Alamos, NM

Magnetic Guiding of Plasma

- Guiding center of charged particles is bound to field lines

Photo: NASA

Macroparticle Removal by Magnetic Filtering

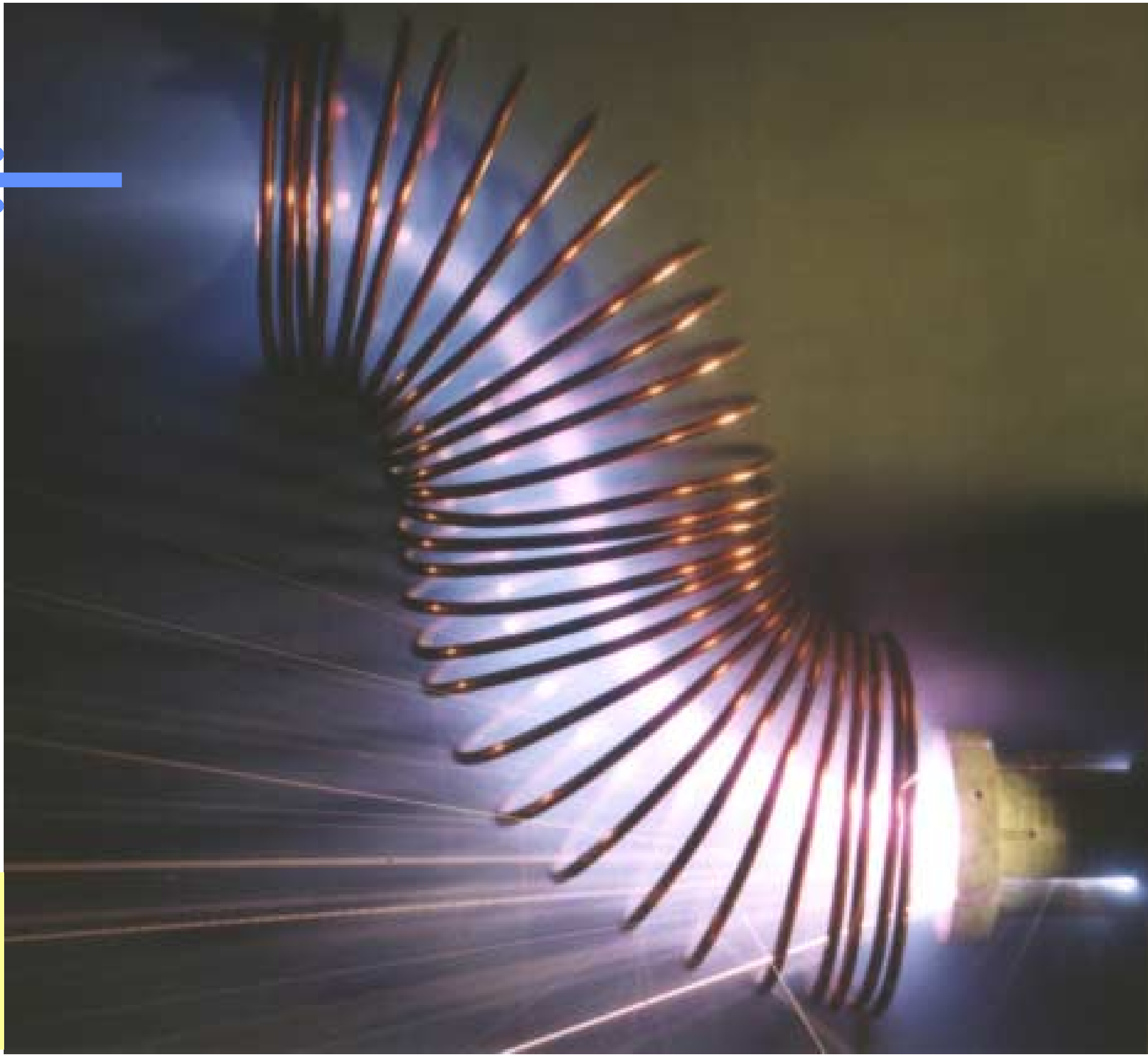


"Classic" 90° Filter Duct

I.Aksenov, *et al.*, *Sov. J. Plasma Phys.* **4** (1978) 425

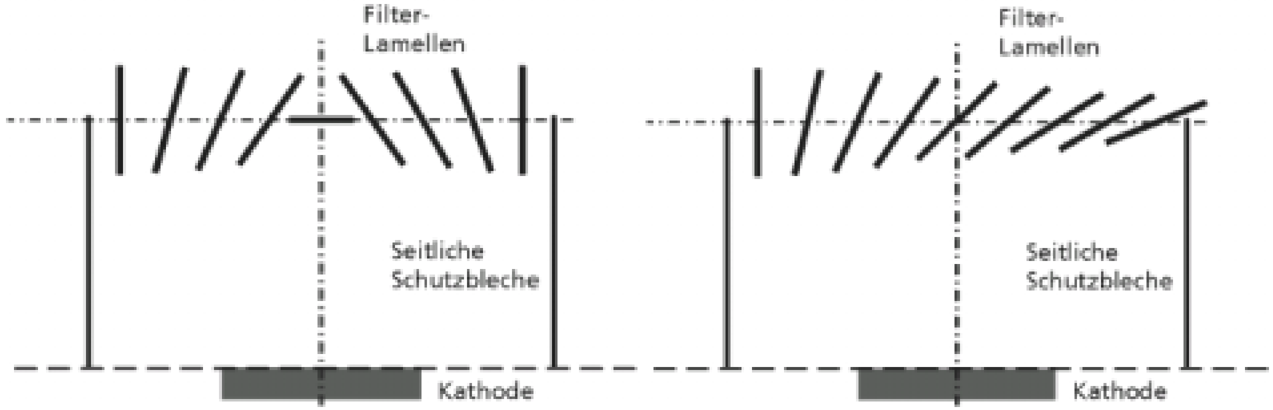
Open Filter for Cathodic Arcs

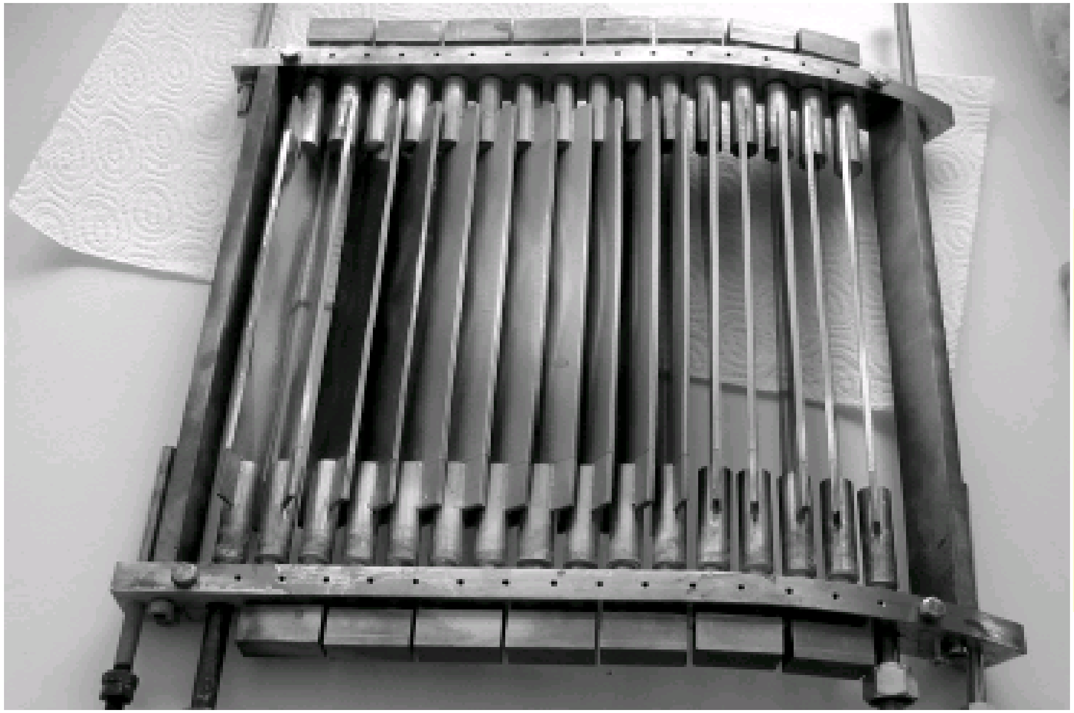
streaming, clean metal plasma



review on filters:
A. Anders, *Surf. Coat. Technol.* **120-121** (1999) 319

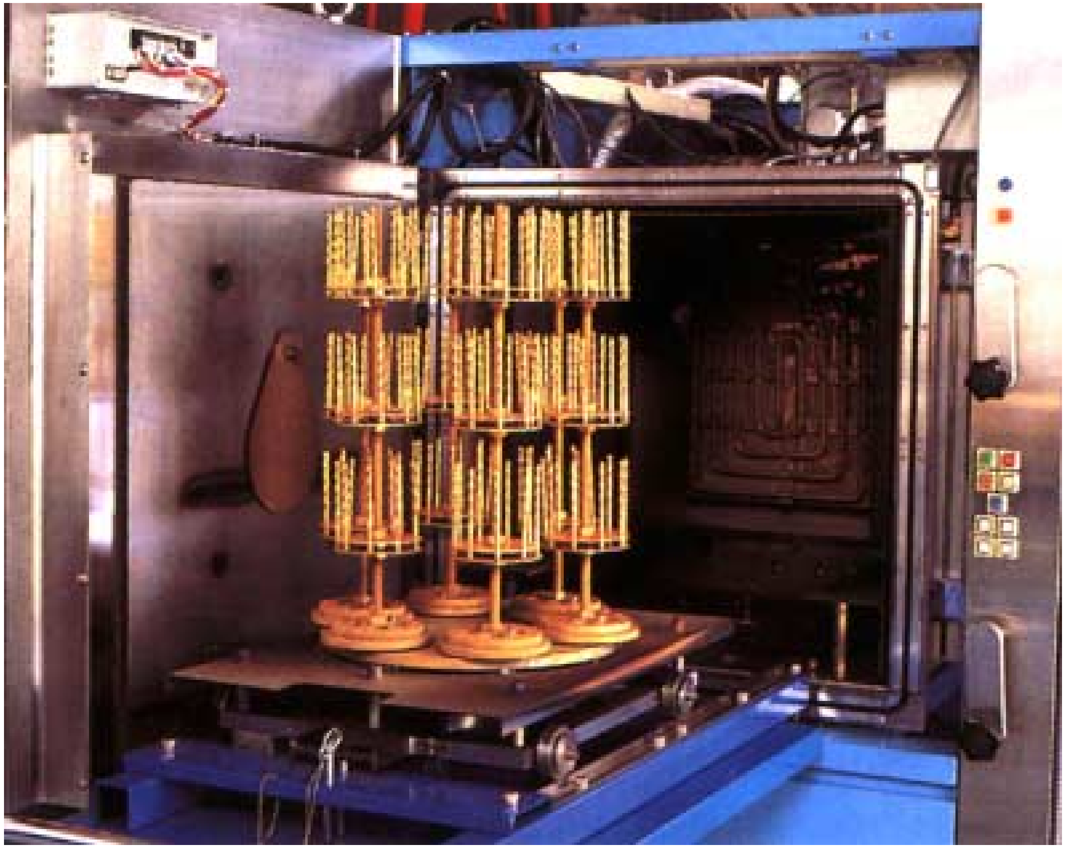
Venetian Blind Filter





• Ryabchikov and Stepanov, *Rev. Sci. Instrum.* **69** (1998) 810
• M. Bilek, *et al.*, *IEEE Trans. Plasma Sci.* **27** (1999) 1202.
• O. Zimmer, PhD Thesis, Ruhr-Universität Bochum, 2002.

Today's Typical Industrial Arc Coating

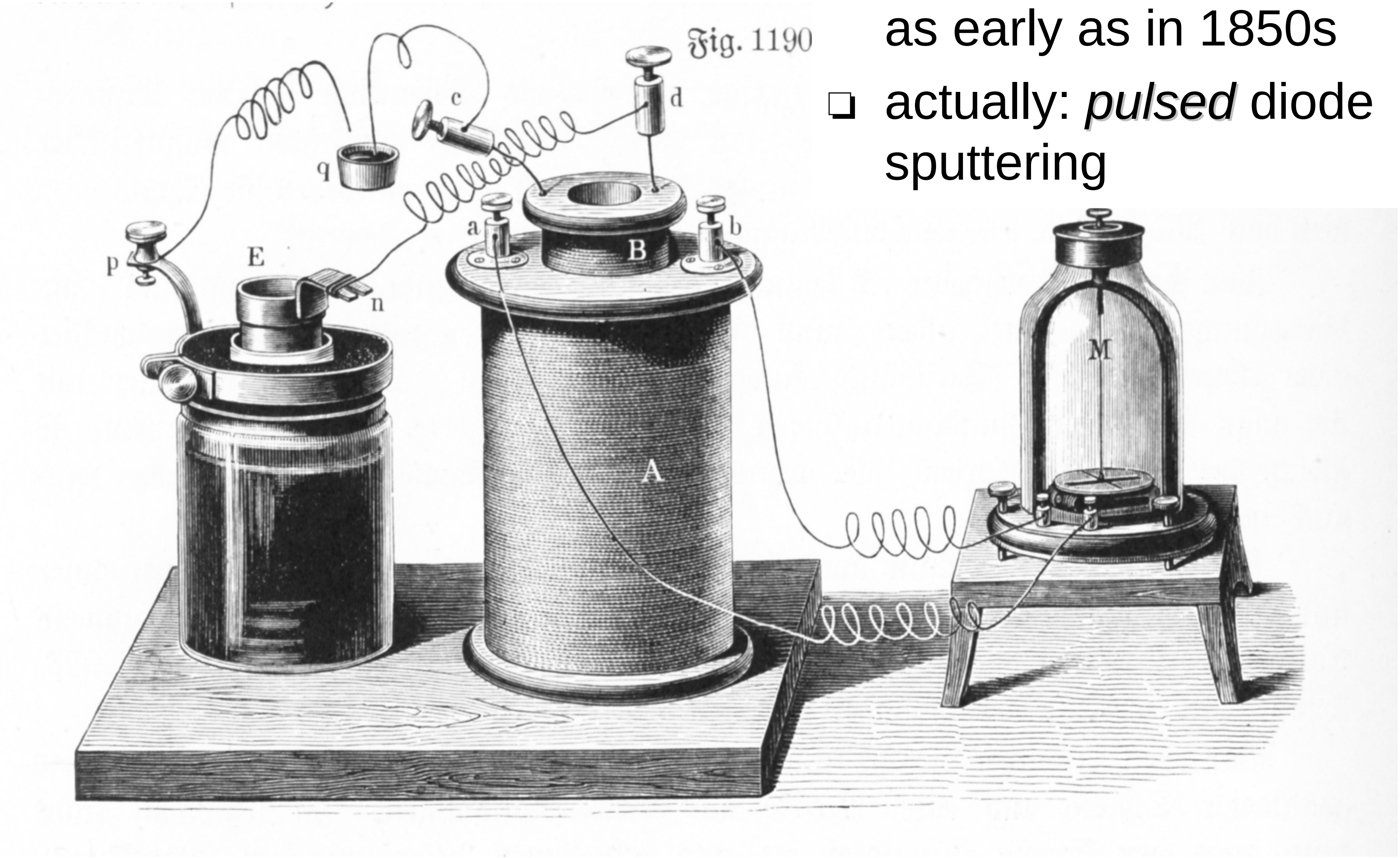


- *example:* TiN or TiAlN on tools; reactive deposition at elevated temperature, unfiltered
- market value added: about $1B/year

Pictures: Cobelco, Japan

Status Part 2: Pulsed Sputtering

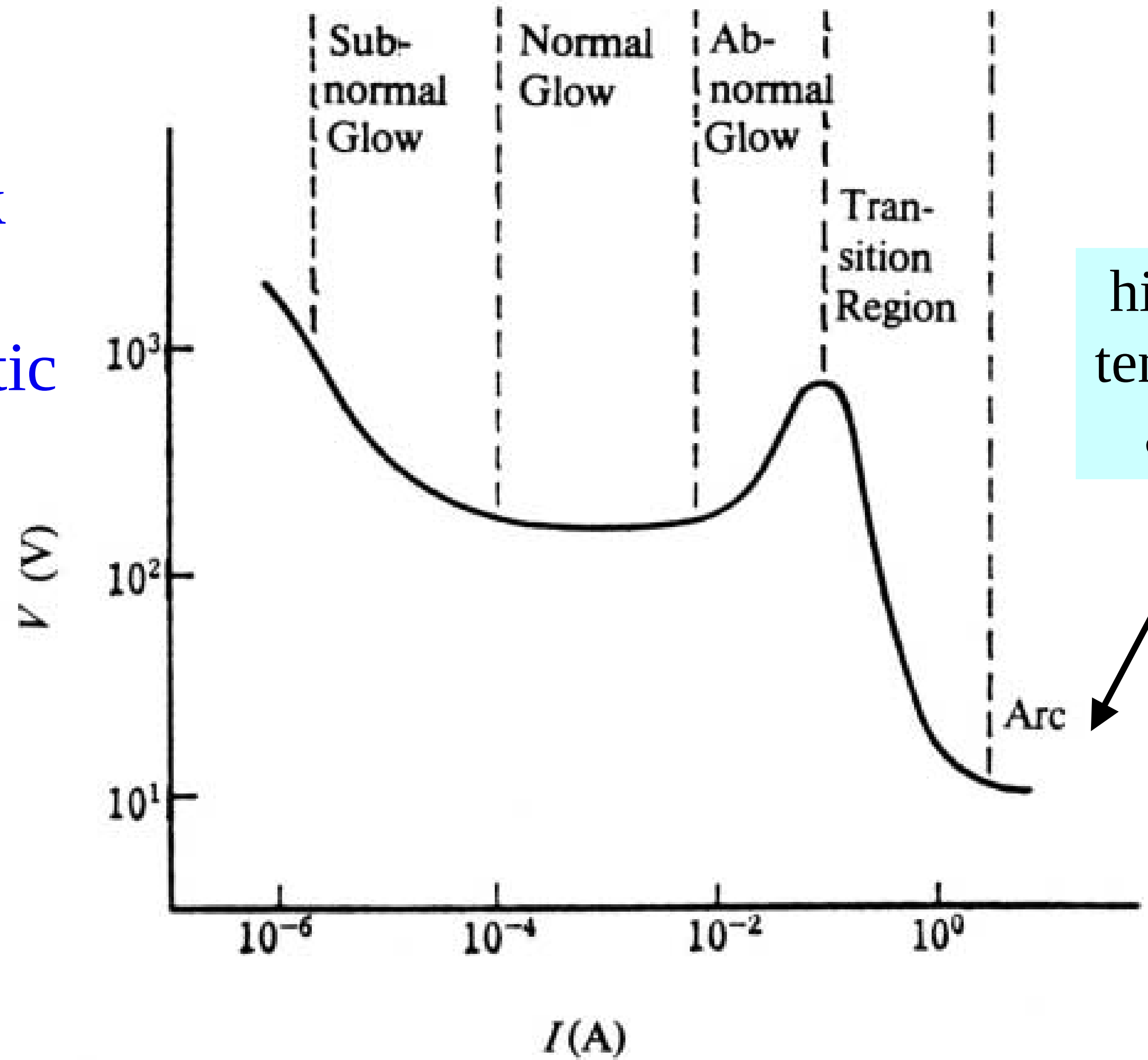
Development of Pulsed Sputtering



- Diode Sputtering observed as early as in 1850s
- actually: *pulsed* diode sputtering

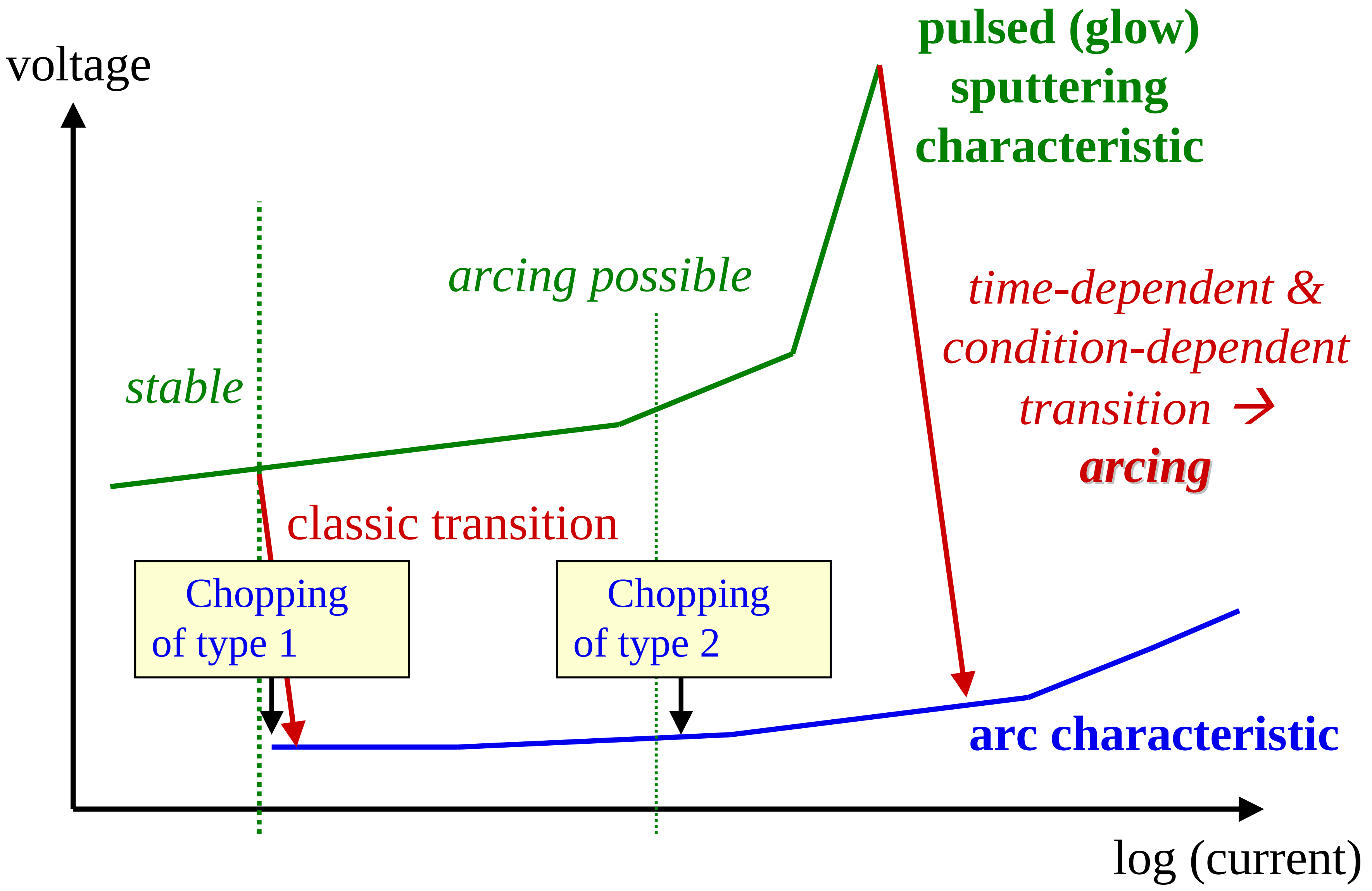
I-V Characteristic for DC Discharges

generic text-book discharge characteristic

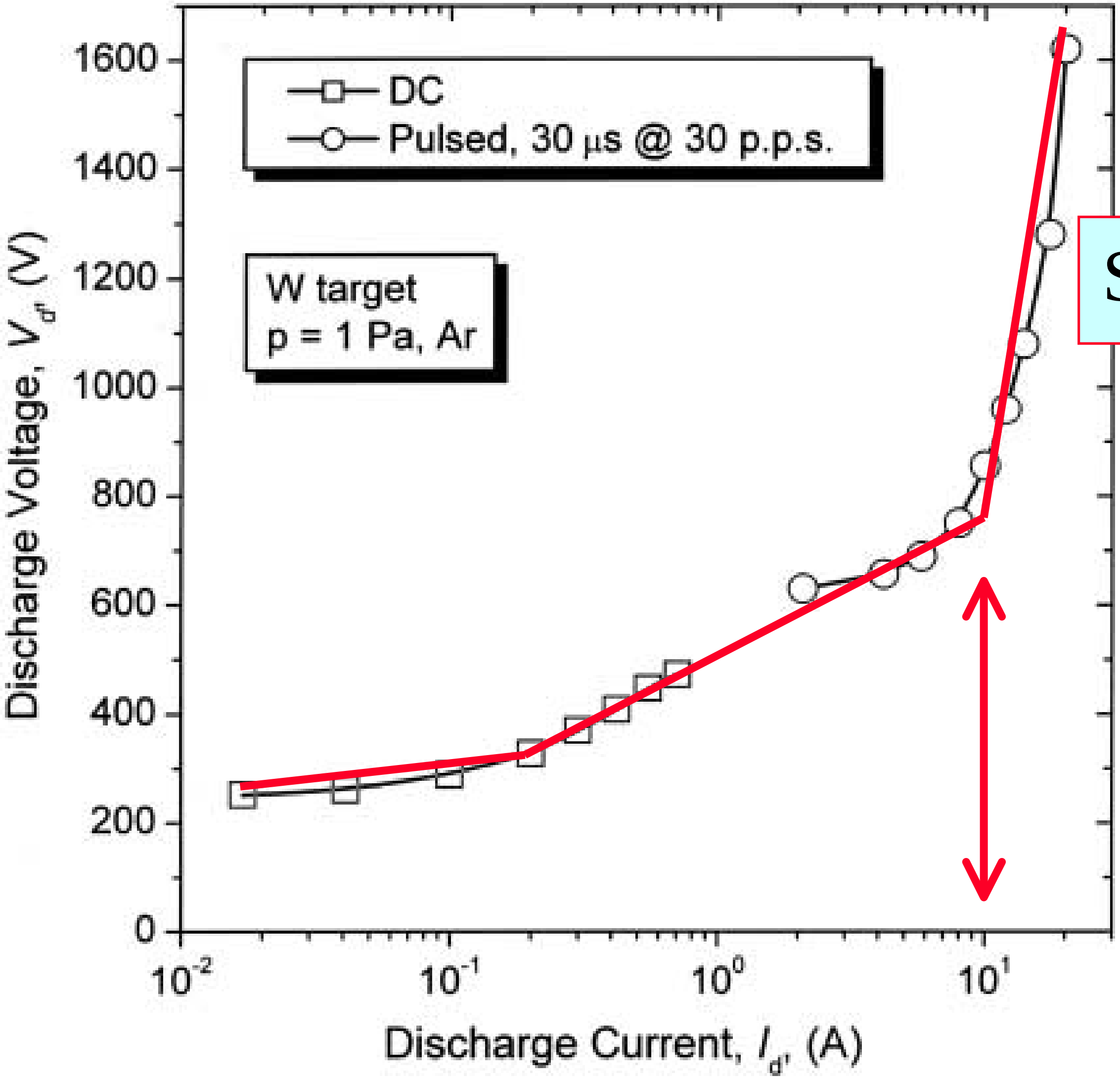


high current tends to be in arc mode

I-V Characteristic and Arcing



Experimental I-V Characteristics



$$I_d = cV_d^q$$

Slope $q \rightarrow 1$

- Anders, *Surf. Coat. Technol.* (2003) in print
- for **Cr** target: Ehiasarian, et al., *Vacuum* **65**, 147 (2002)

Types of Pulsed Sputtering

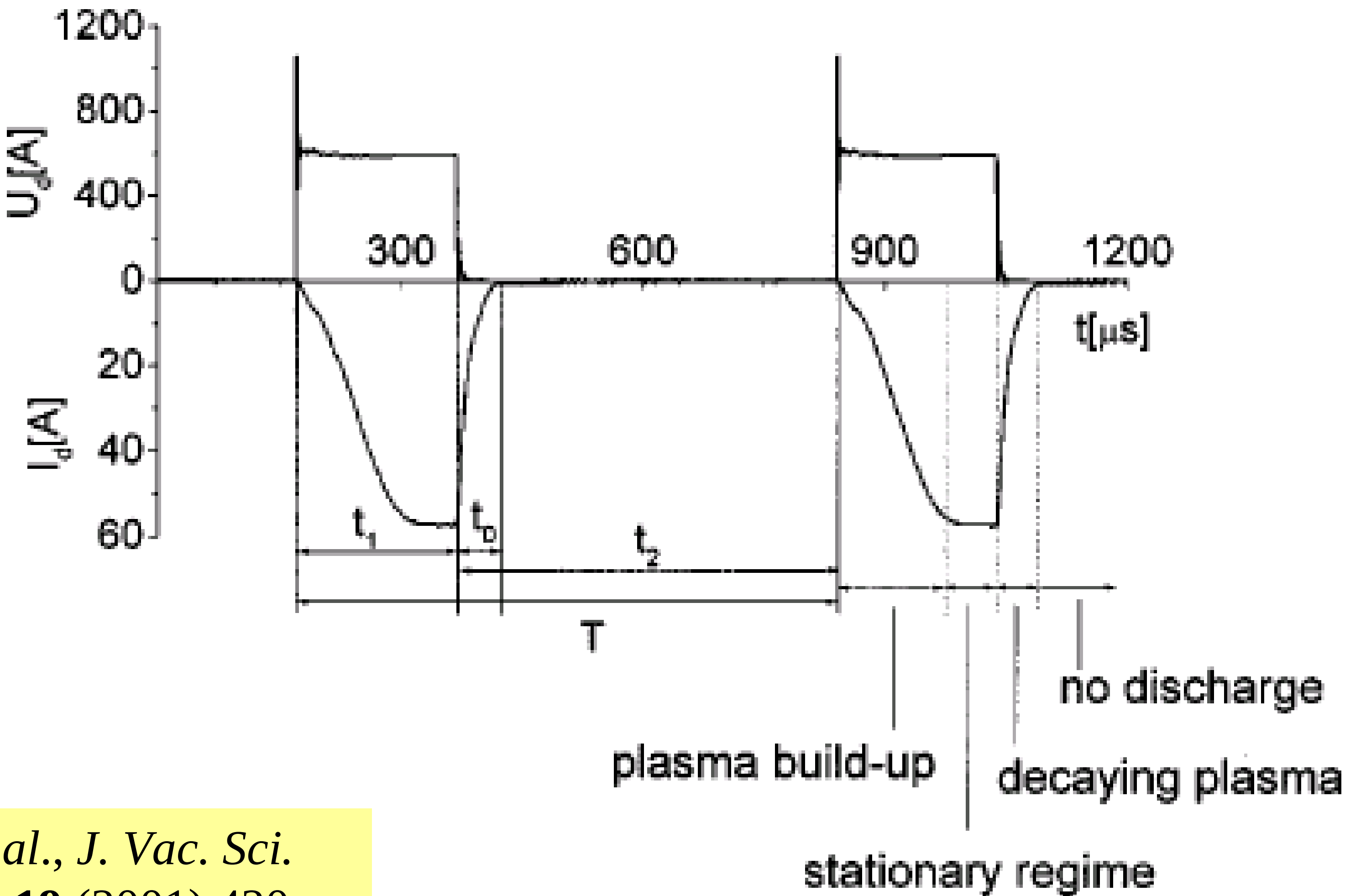
- **Medium-Frequency, "Medium"-power pulsed sputtering**
  - Developed in the 1990s
  - Unipolar or bi-polar DC pulsed
  - Medium frequency (high duty cycle): 10-350 kHz
  - "Medium" pulsed power and current density:
    - Up to several 100 W/cm^2 (peak)
    - Up to several 100 mA/cm^2 (peak)

Limitations by
- average power / cooling
- arcing
- power supply

- **High Power Pulsed Sputtering**
  - Introduced in late 1990s
  - Low frequency (< 1 kHz); low duty cycle
  - Very high power and current density
    - Several 1000 W/cm^2 (peak)
    - Several 1000 mA/cm^2 (peak)

Types of Pulsed Sputtering: Pulsed, Medium-Frequency Sputtering

- **Example:**



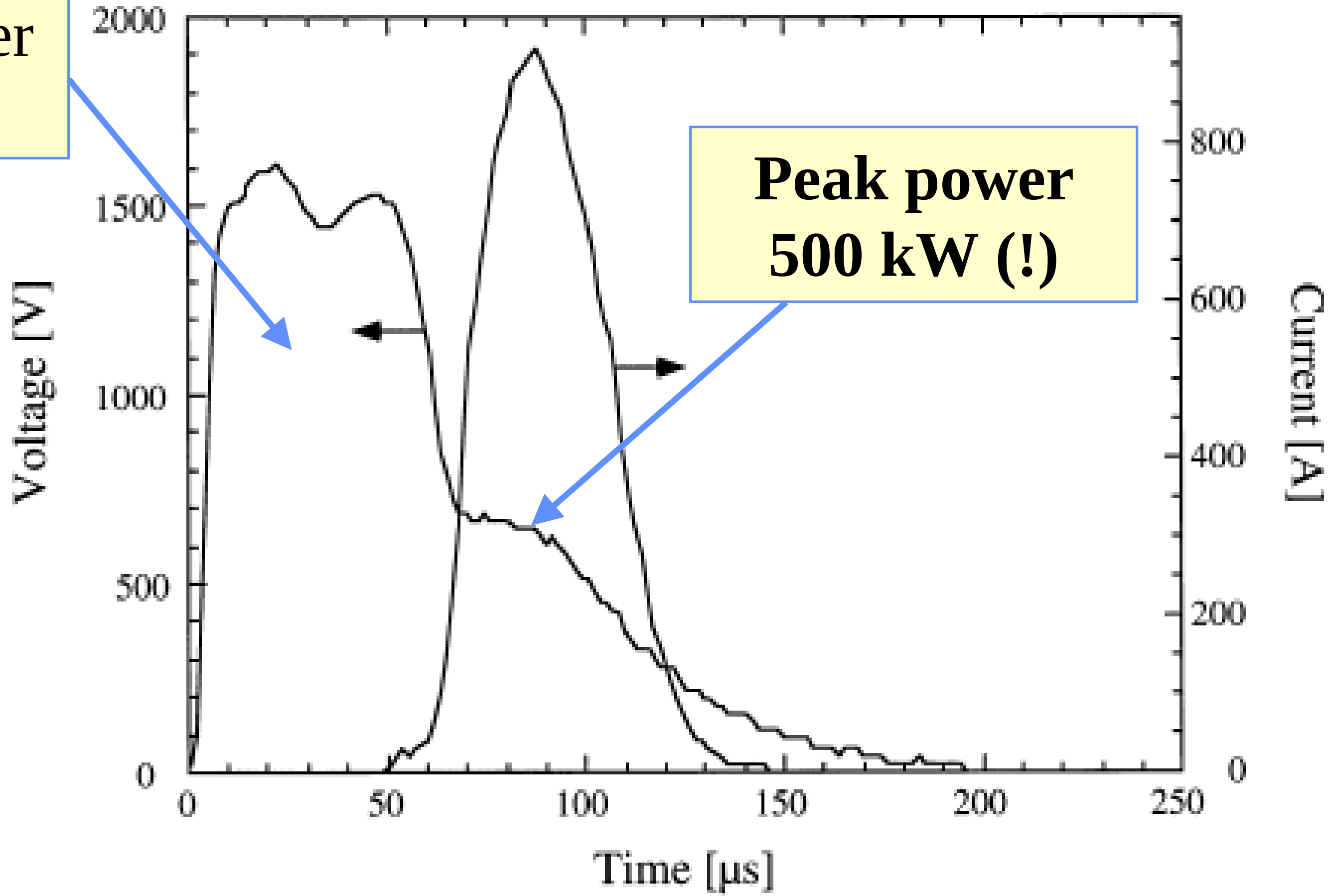
J. Musil, *et al.*, *J. Vac. Sci. Technol. A*, **19** (2001) 420

Types of Pulsed Sputtering: High Power Pulsed Sputtering

Cu target, 65 mPa Ar

Delay: no simmer discharge

Peak power 500 kW (!)

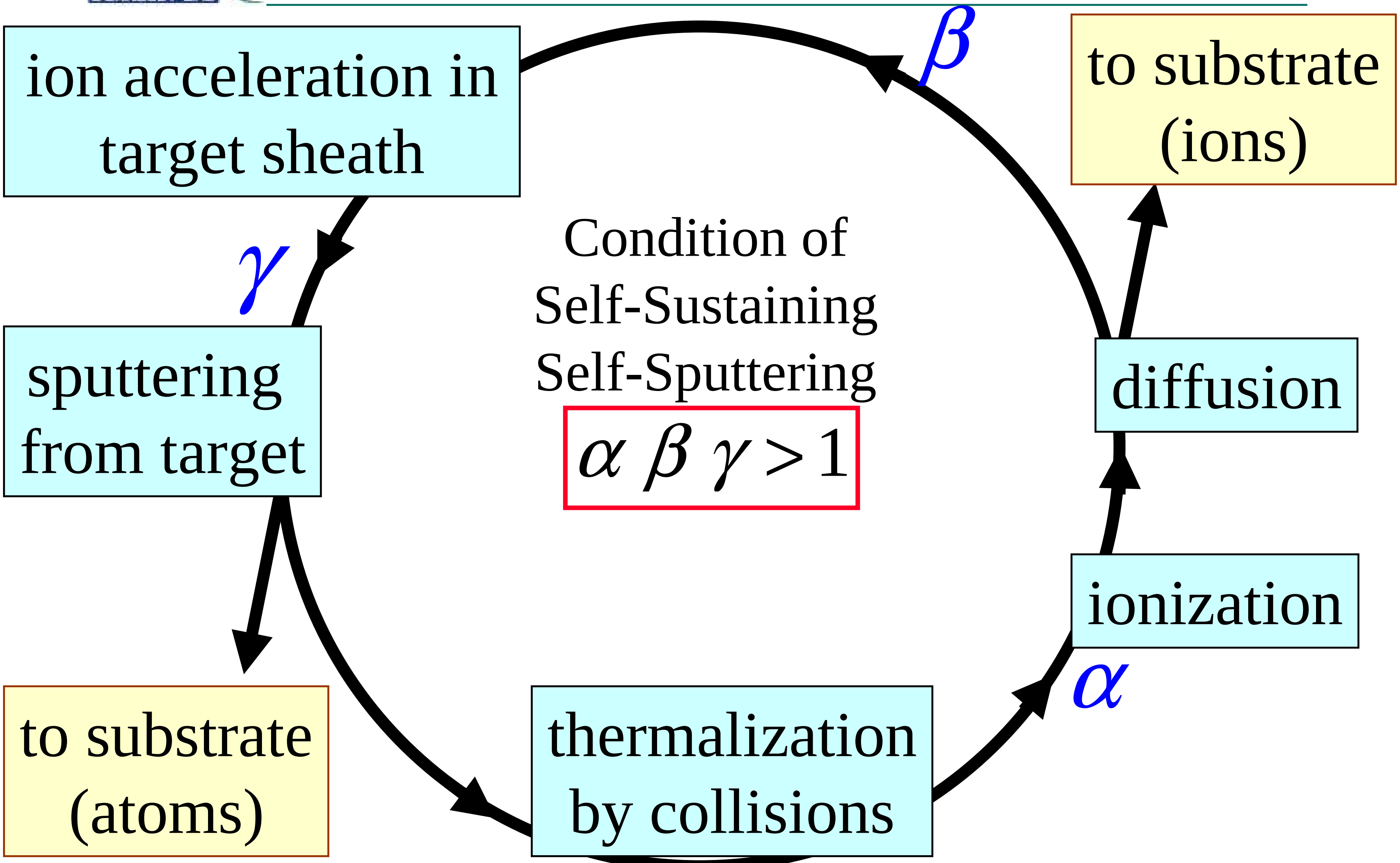


V. Kouznetsov, *et al.*, *Surf. Coat. Technol.* **122**, 290-293 (1999)

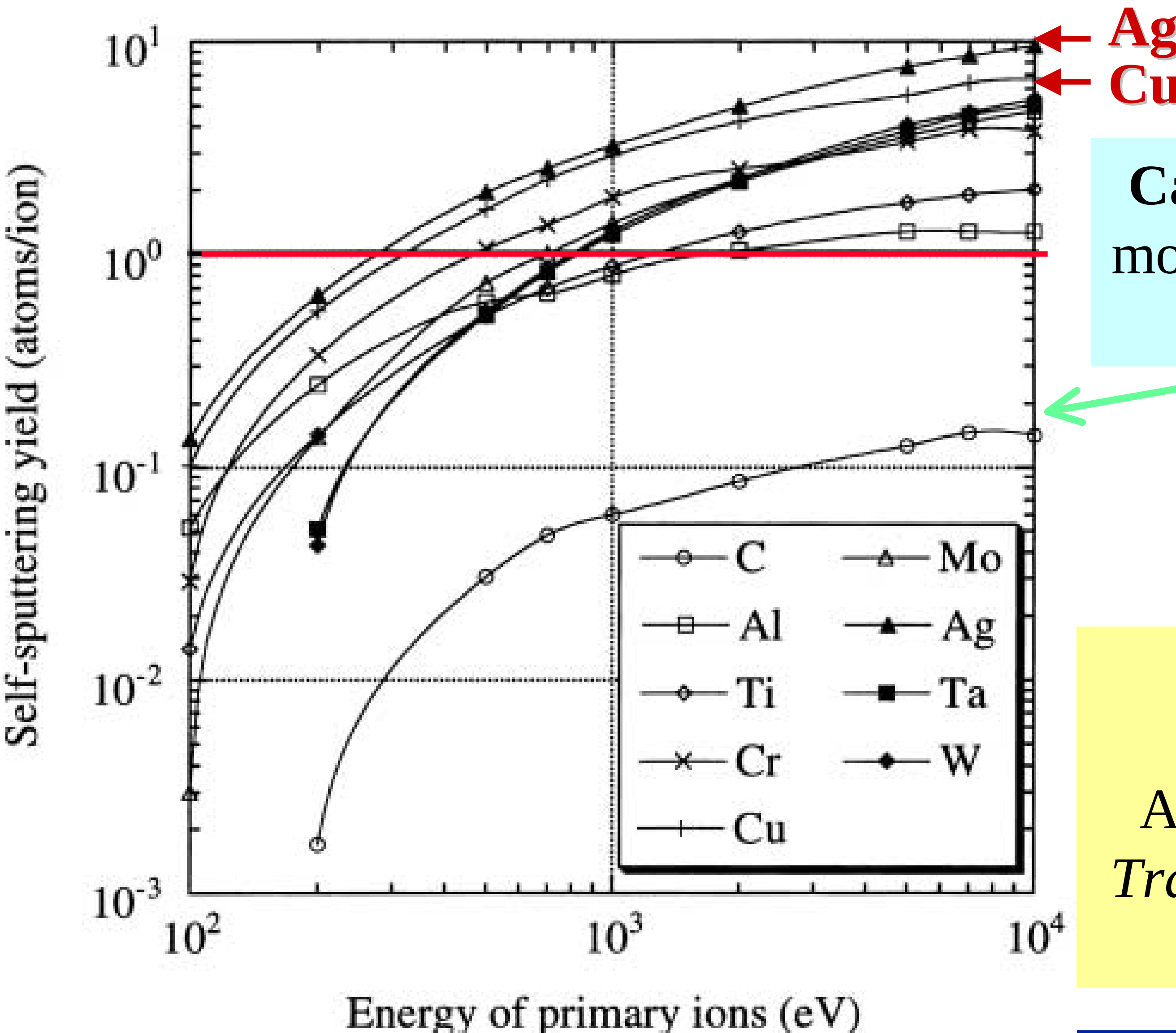
High Power Pulsed Sputtering

- Proposed by Kouznetsov and co-workers in late 1990s
- use of traditional sputter magnetron
- increase power during pulses by > 2 orders of magnitude
- average power is within acceptable level by using low duty cycle
- observe increased degree of ionization by
  - Optical spectroscopy
  - Charge-to-mass spectrometry
  - Biased quartz-crystal balance technique

Self-Sputtering



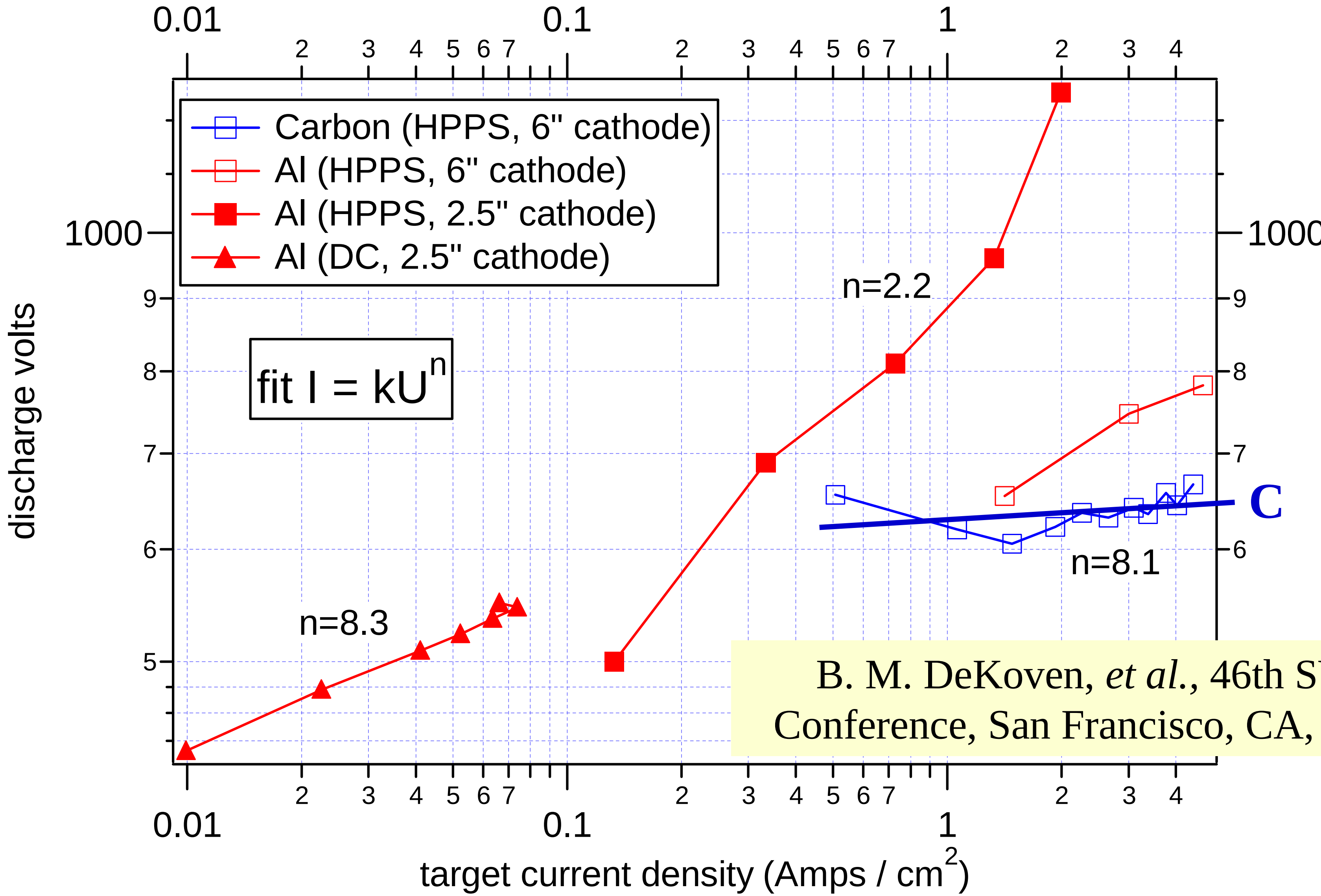
Self-Sputter Yield



Carbon cannot go in mode of self-sustained self-sputtering

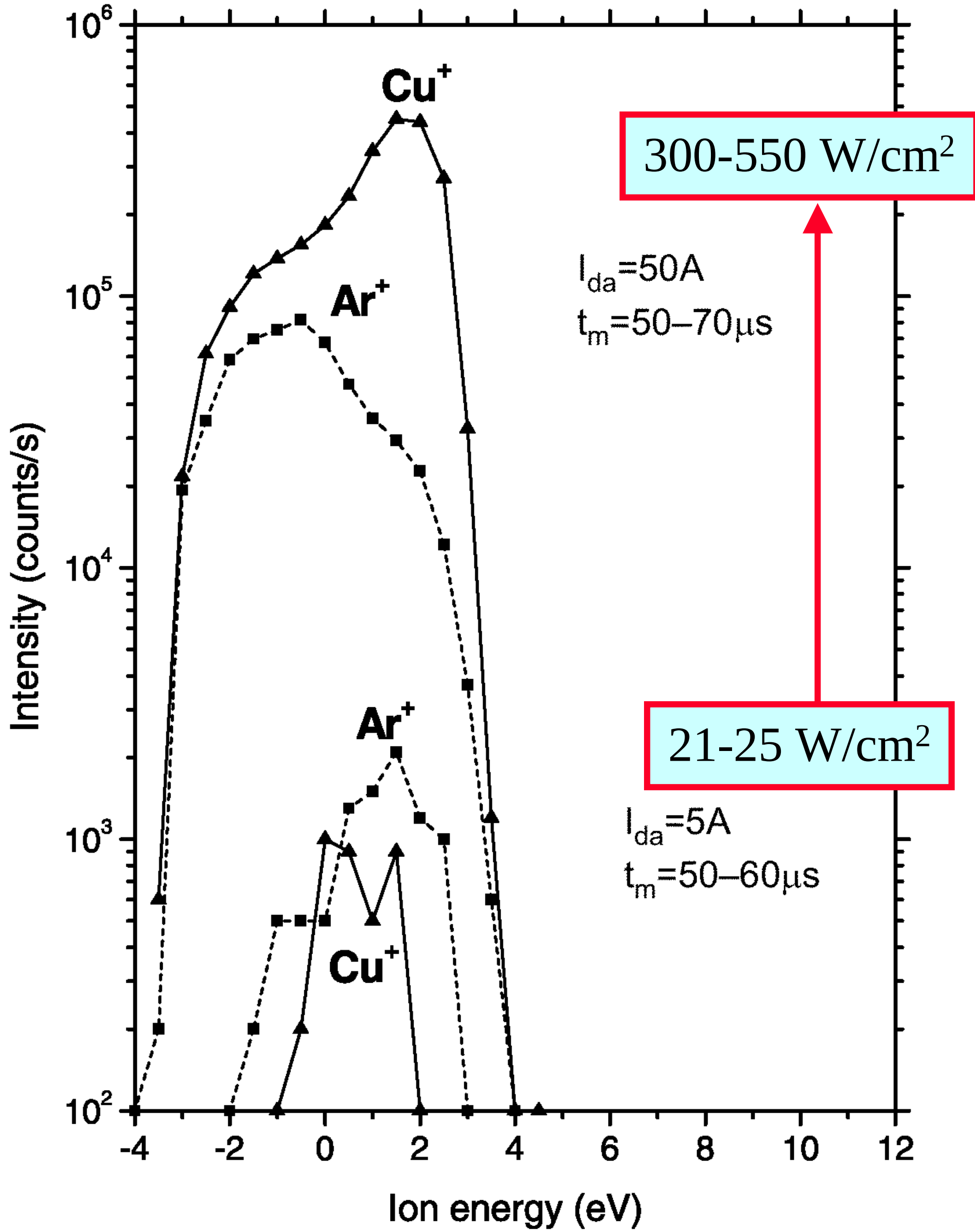
Monte Carlo Simulations
Anders, *et al*, *IEEE Trans. Plasma Sci.* **23** (1995) 275

Current-Voltage Characteristic for High Power Pulsed Sputtering



B. M. DeKoven, *et al.*, 46th SVC Conference, San Francisco, CA, 2003.

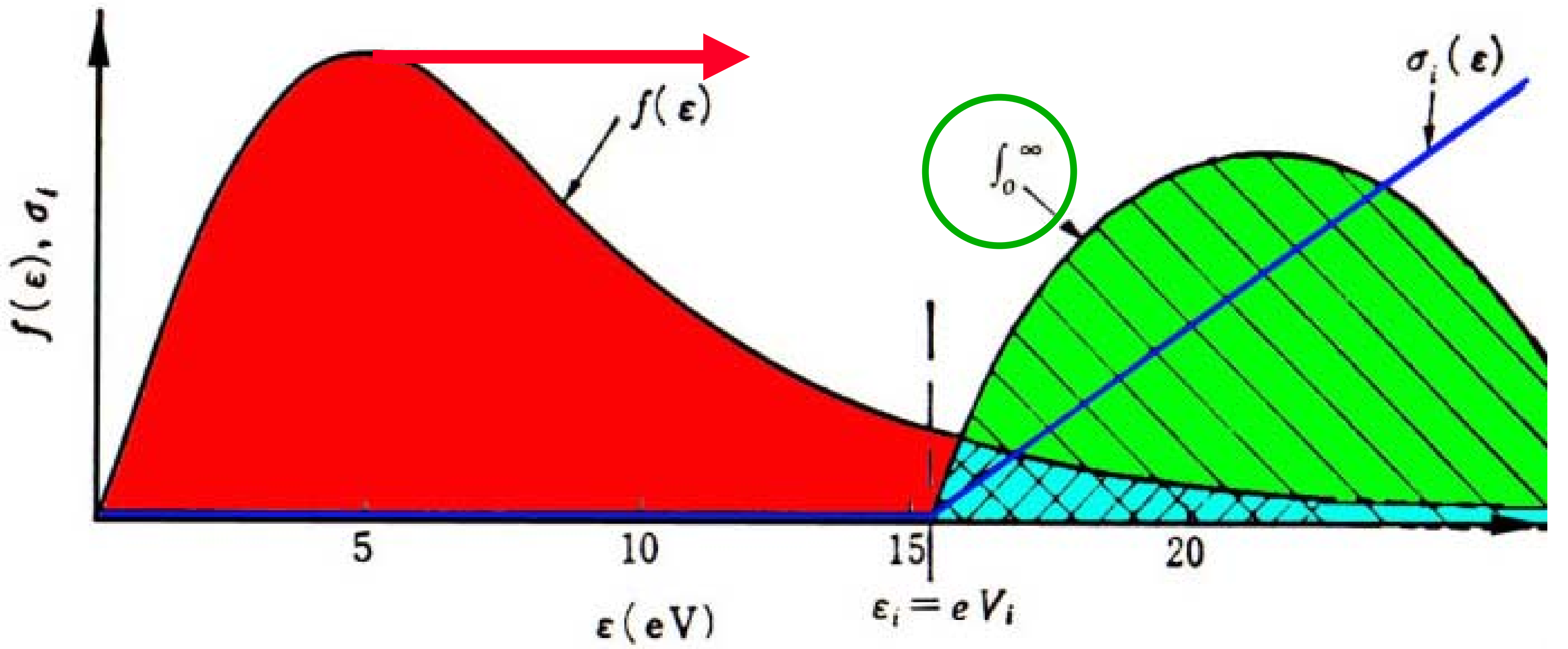
- Example: Cu target, ion energy measurements
- Ionization of sputtered material
- for Cu [and Ag] even at moderate power density and high frequency!



Vlcek, Pajdarova, Musil, *Contrib. Plasma Phys.* (2003)

Distribution Functions and Rate Coefficients

Mean free path $\lambda_{\alpha} = \left(\sum_{\beta} n_{\beta} \sigma_{\alpha\beta} \right)^{-1}$



Interpretation of Child Law (1911) for Plasma Sheath

Poisson equation

$$\boxed{\varepsilon_0 \nabla \bullet \mathbf{E} = \rho}$$

Child current

$$\boxed{j_i = \frac{4}{9}\varepsilon_0 \left(\frac{2e}{m_i}\right)^{1/2} \frac{V_0^{3/2}}{s^2}}$$

Space charge limited current

↓

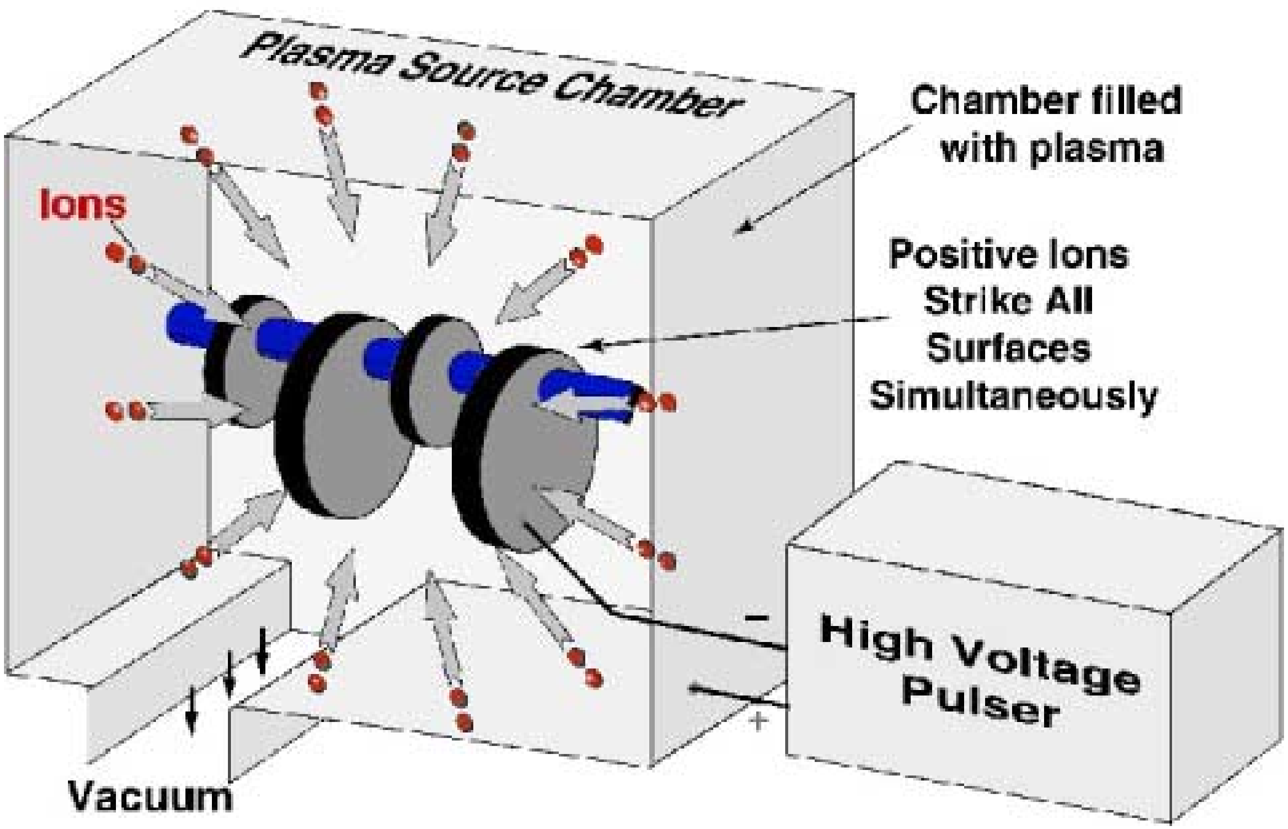
self-adjusting sheath
(Child Sheath)

$$\boxed{s_{Child} = \frac{\sqrt{2}}{3}\lambda_{De}\left(\frac{2eV_0}{kT_e}\right)^{3/4}}$$

Plasma density increases → Sheath thickness decreases

Transient Sheath

- Resource: PIII theory.
- conformal ion implantation of plasma ions by acceleration in high voltage sheath



Sheath Development

• If pulse rise is slow: $\tau_{rise} = t_{rise}\omega_{pl,i} > 1$

↓

Ion matrix sheath does not exist but *time-depended Child sheath*.

Examples of dimensionless parameters

• If pulse sequence is fast $\tau_{off} = t_{off} / t_{restore} < 1$

↓

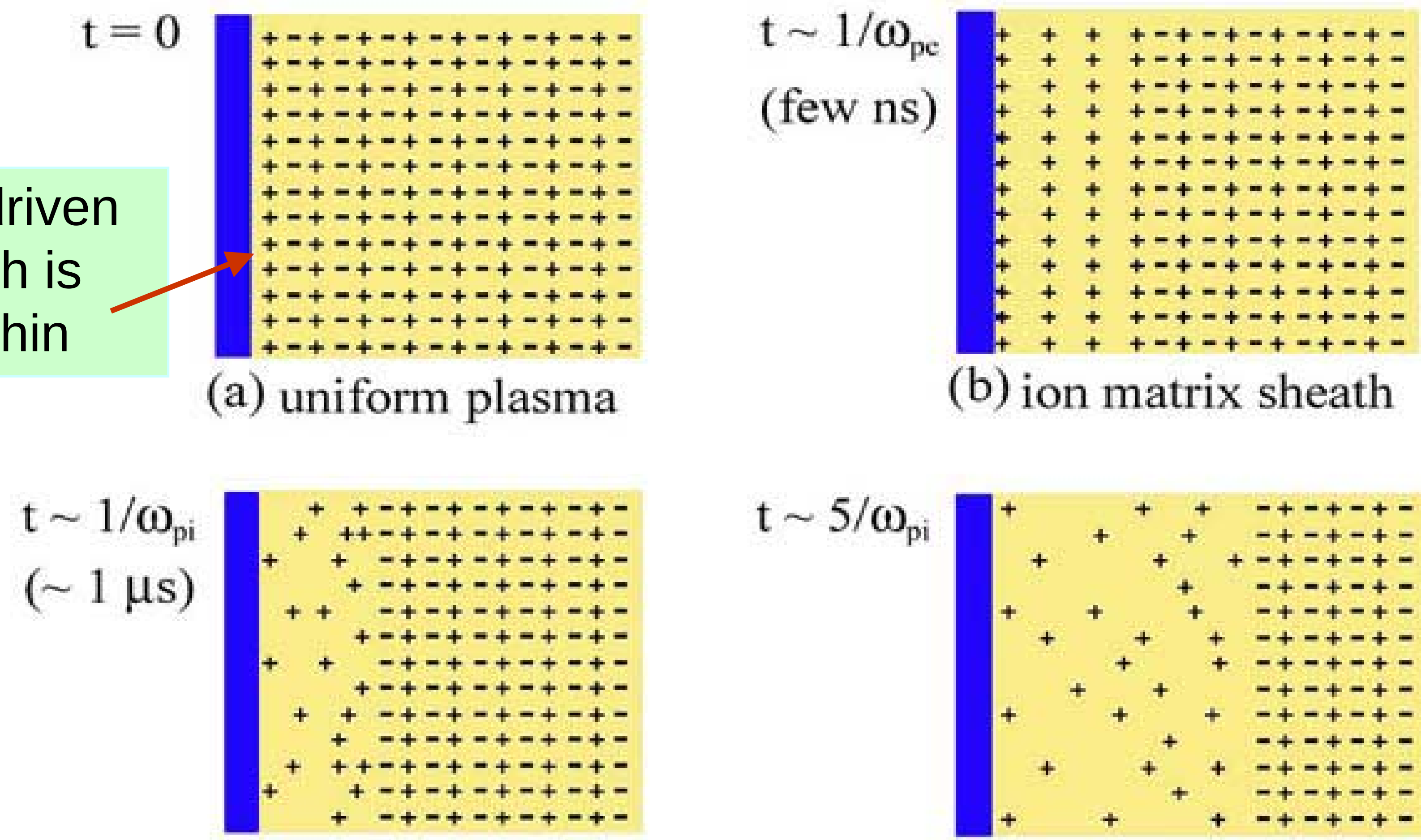
where $t_{restore} \approx \dfrac{s_{Child}^2}{D_{ambi}}$

Multiple-pulse effects exist.

$D_{ambi} \approx kT_e \mu_i / e$

Sheath Development

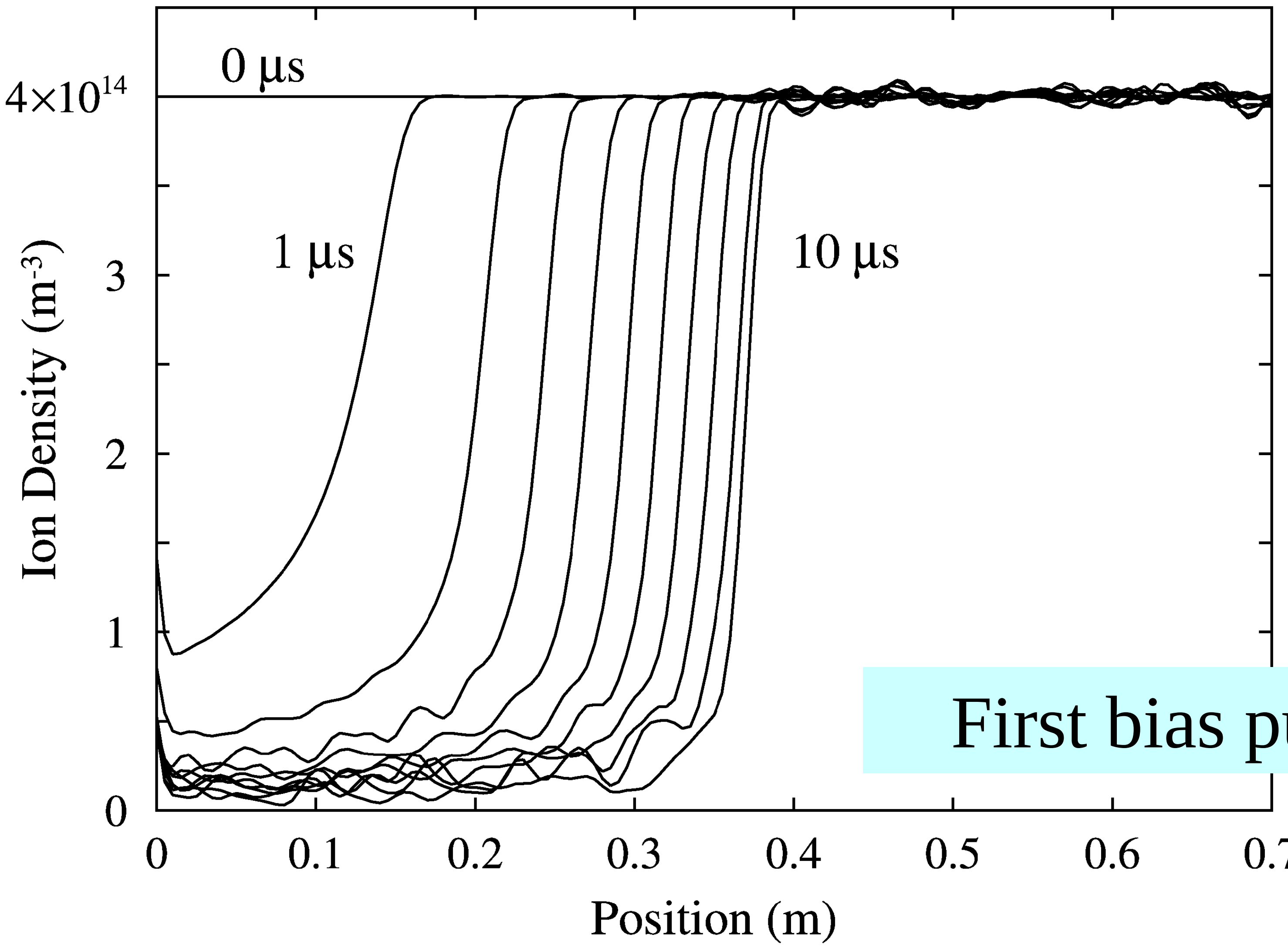
non-driven sheath is very thin



Application of dimensionless parameters:

Ion matrix sheath exists only if $\tau_{rise} = t_{rise}\omega_{pl,i} < 1$

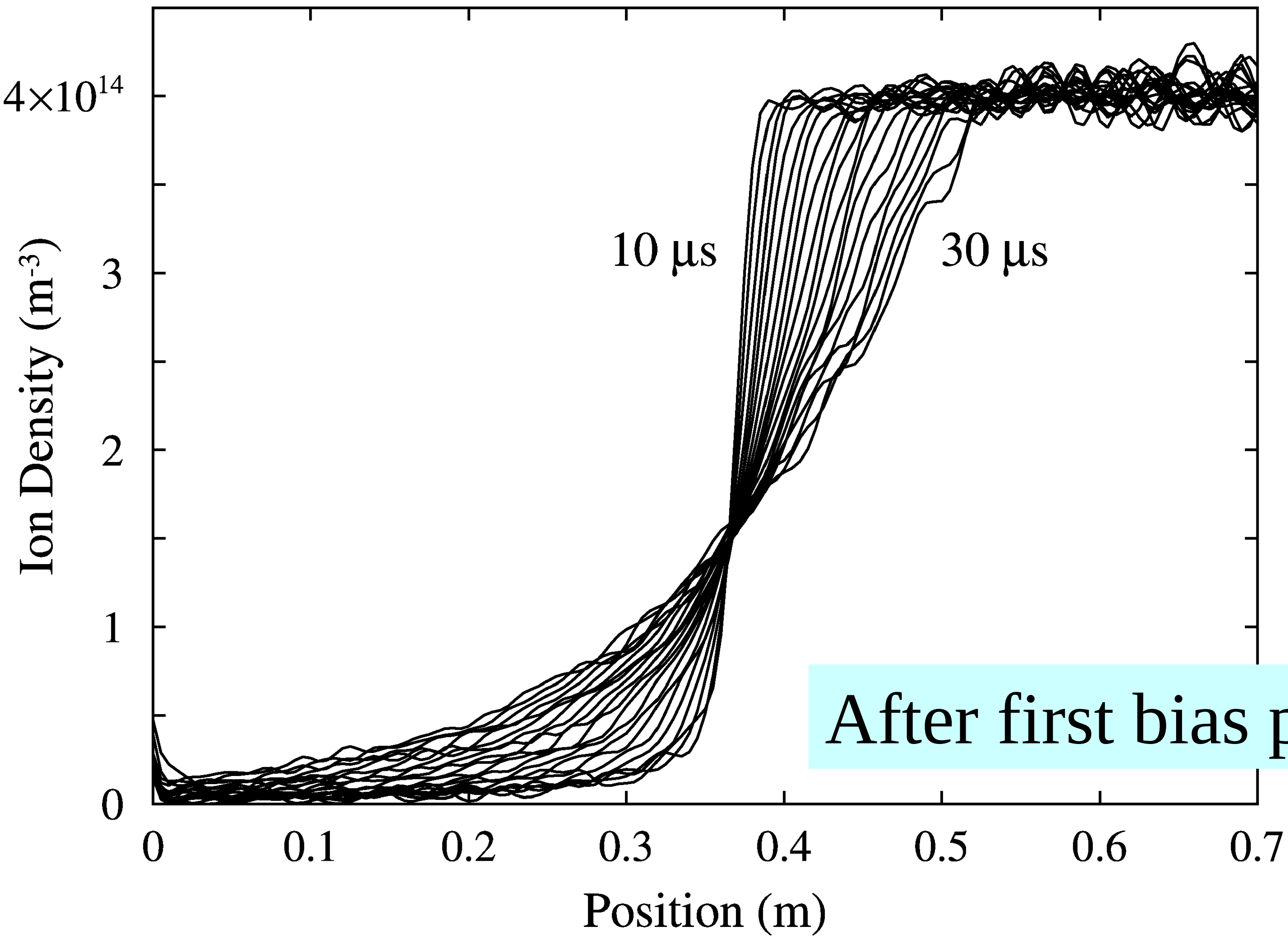
Transient Sheath: PIC Simulations



First bias pulse

B. Wood, in: Anders (Ed.), *Handbook of PIII&D*, Wiley, N.Y. 2000

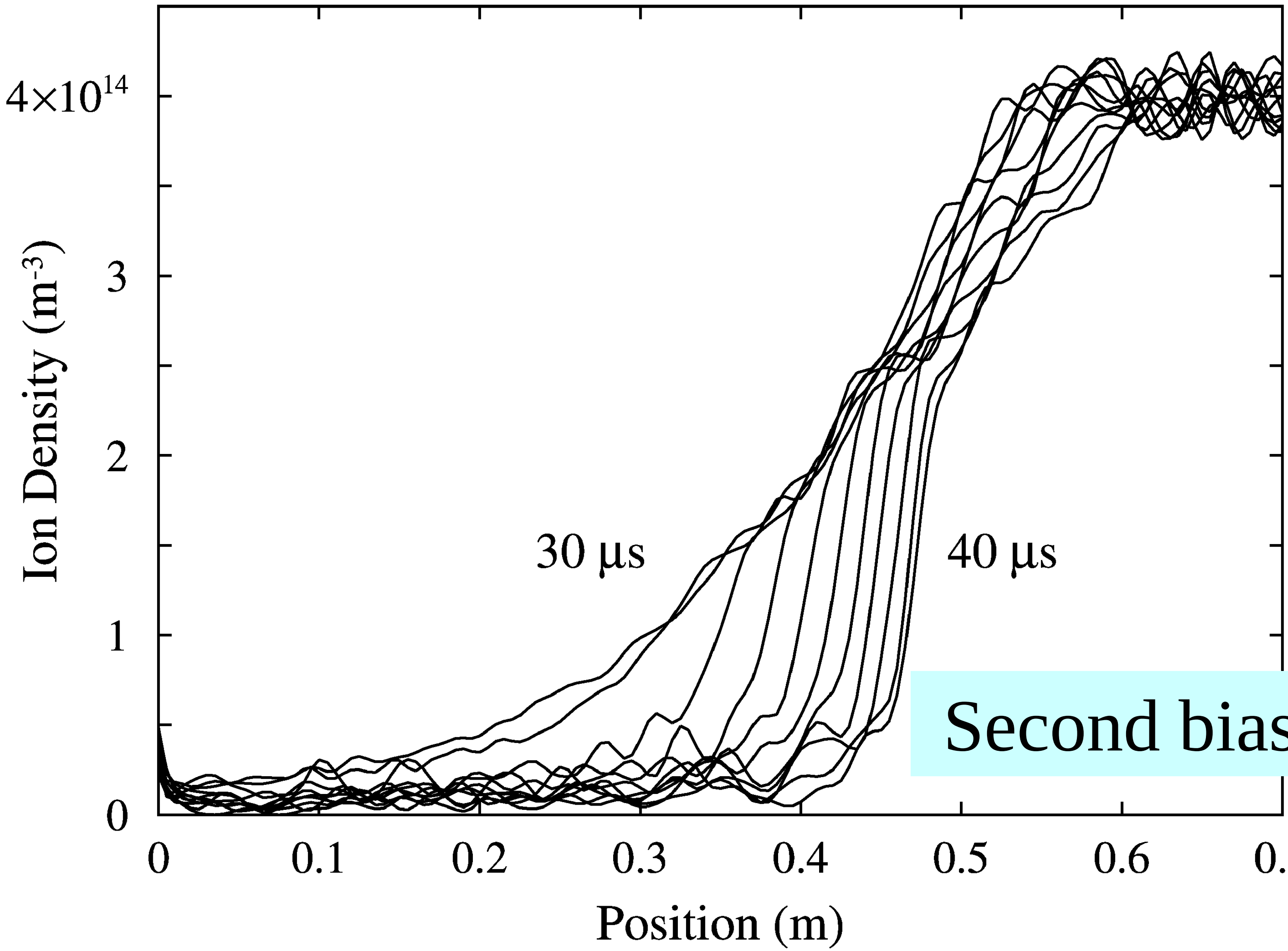
Transient Sheath: PIC Simulations



After first bias pulse

B. Wood, in: Anders (Ed.), *Handbook of PIII&D*, Wiley, N.Y. 2000

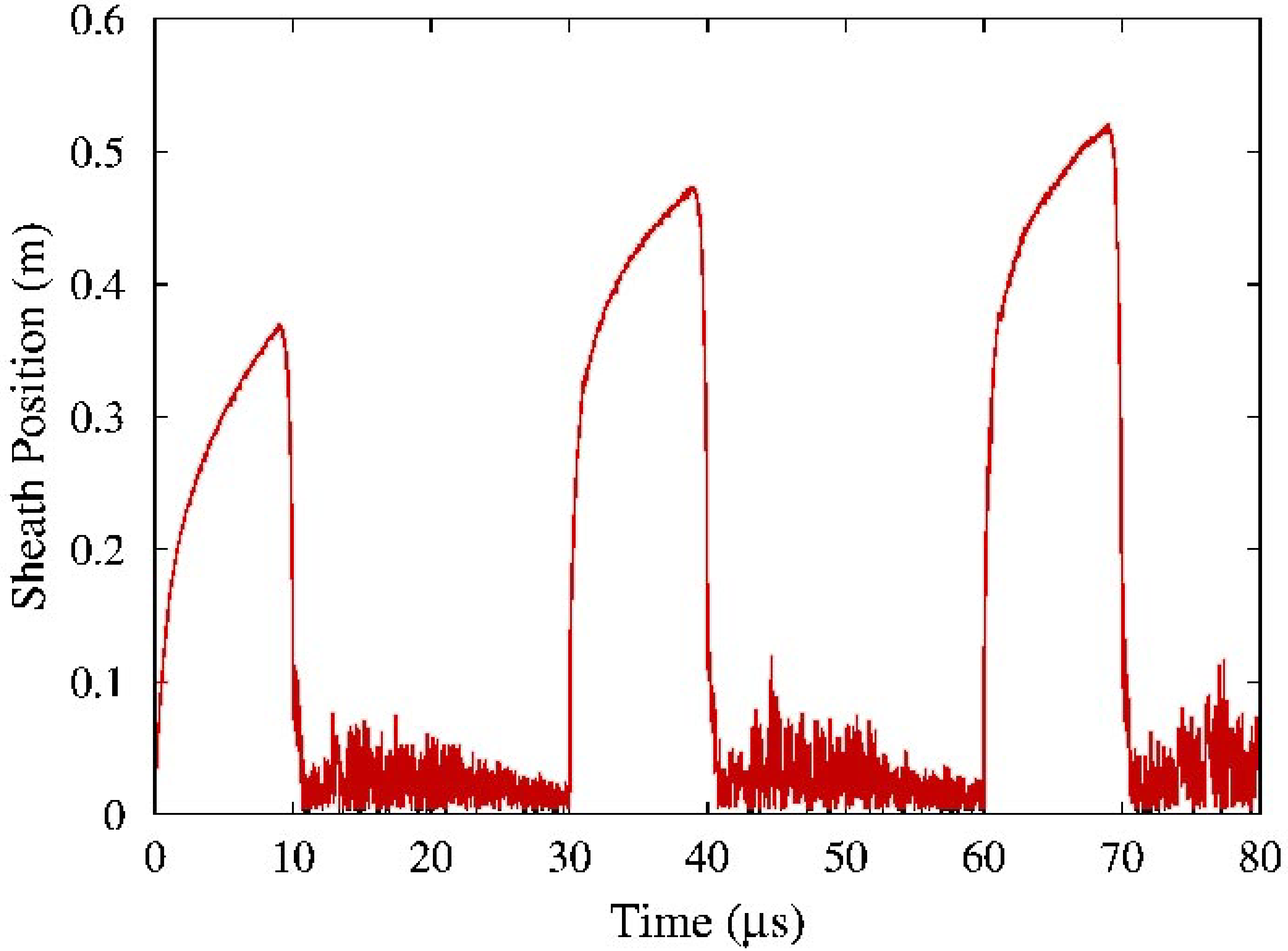
Transient Sheath: PIC Simulations



Second bias pulse

B. Wood, in: Anders (Ed.), *Handbook of PIII&D*, Wiley, N.Y. 2000

Multiple-Pulse Effects at High Duty Cycle



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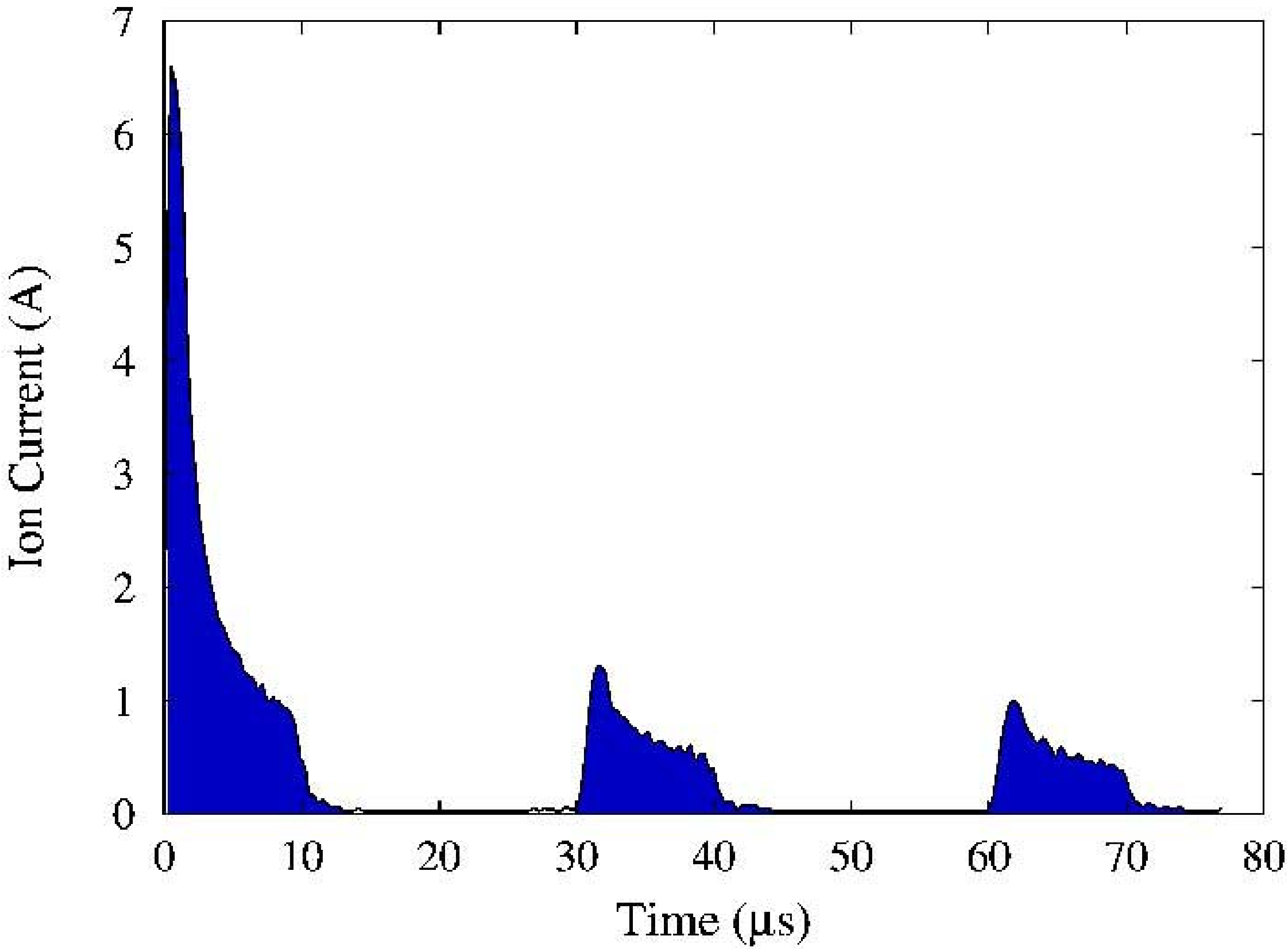
Multiple-Pulse Effects at High Duty Cycle



B. Wood, in: Anders (Ed.), *Handbook of PIII&D*, Wiley, N.Y. 2000

Ongoing and Future Developments. Vision

Ongoing and Future Developments Vision

- **Cathodic arcs**
  - Improved filters
  - Research in filtered, reactive arc deposition
  - Large area coating, linear sources
  - Use of advanced biasing (plasma immersion deposition)
- **Pulsed Sputtering**
  - Research in ionization enhancement
  - Control, limitation, elimination of arcing
  - Scaling to larger areas
  - Use of advanced biasing (plasma immersion deposition)
- **For both:**
  - Graded (multi-)functional films
  - Stress-controlled films
  - Nanostructures
  - Bio-compatible coatings and structures

Out-of-plane, double-bent filter

- Out-of-plane double-bent filter from Nanyang Technical University Singapore
- closed architecture
- commercial version

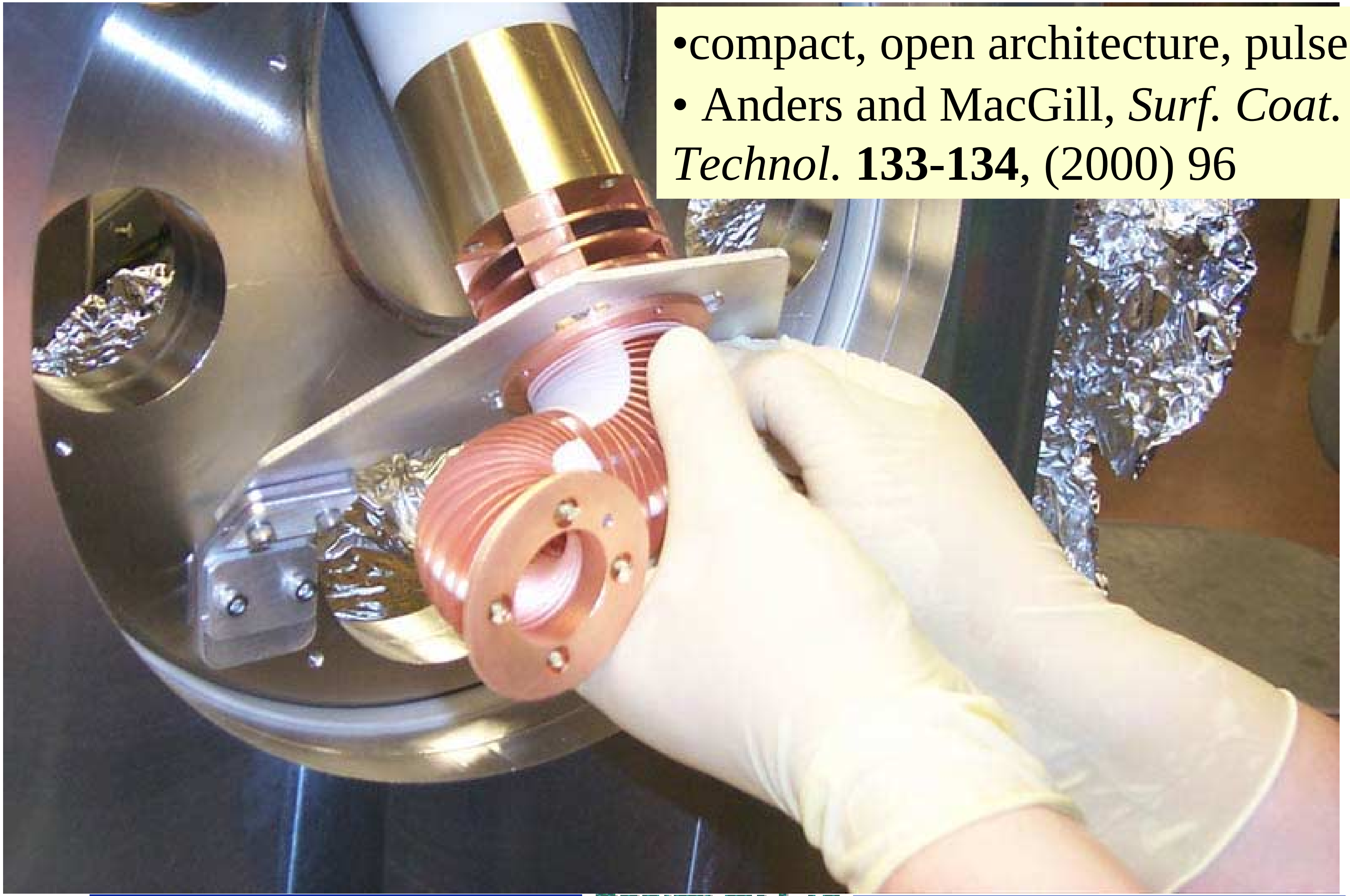
  Shimadzu DLC-MR3CA

X. Shi et al., *Thin Solid Films* **345** (1999) 1

Twist Filter

•compact, open architecture, pulsed

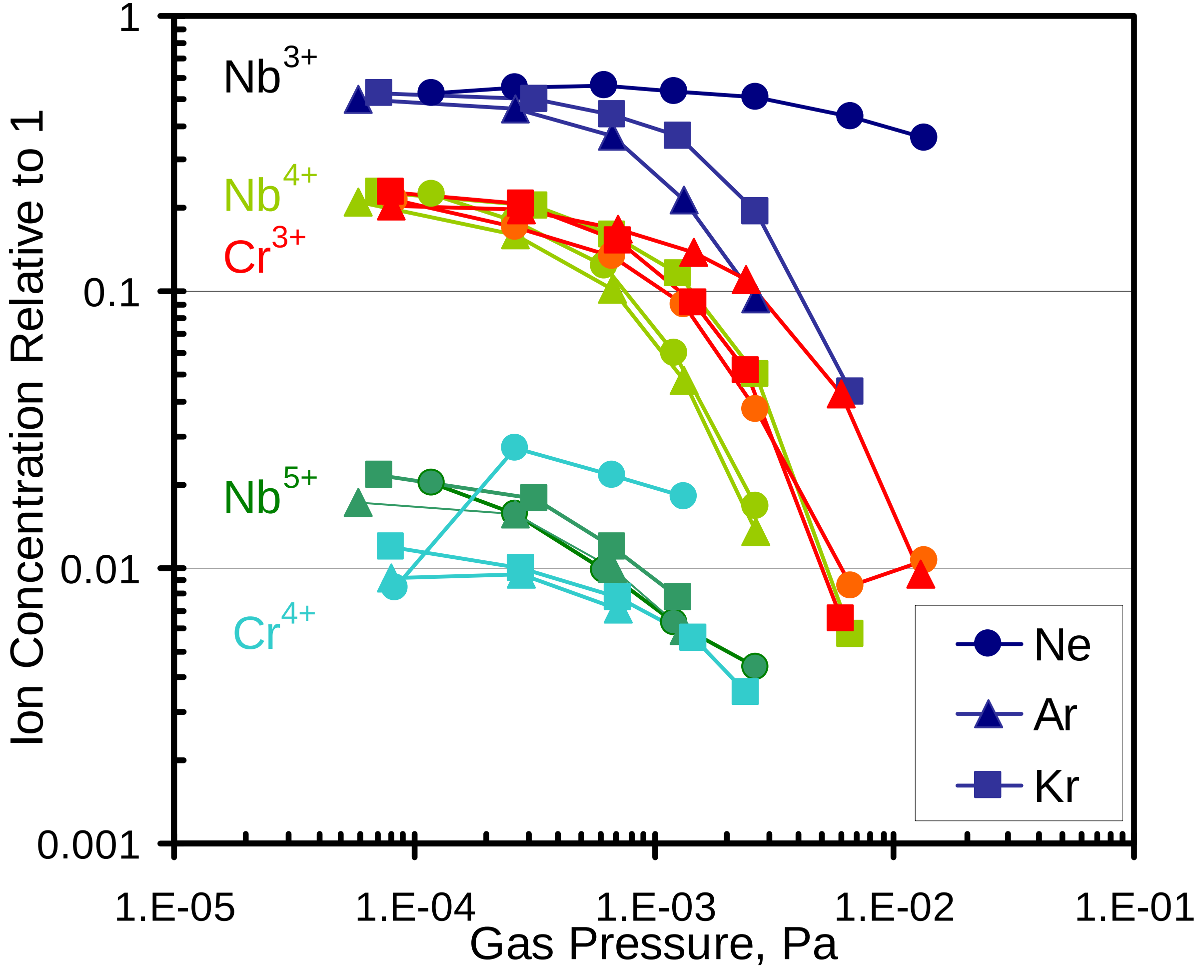
• Anders and MacGill, *Surf. Coat. Technol.* **133-134**, (2000) 96



Effect of Noble Gases on Ion Charge States

Metal Ion Charge States ≥ 3+

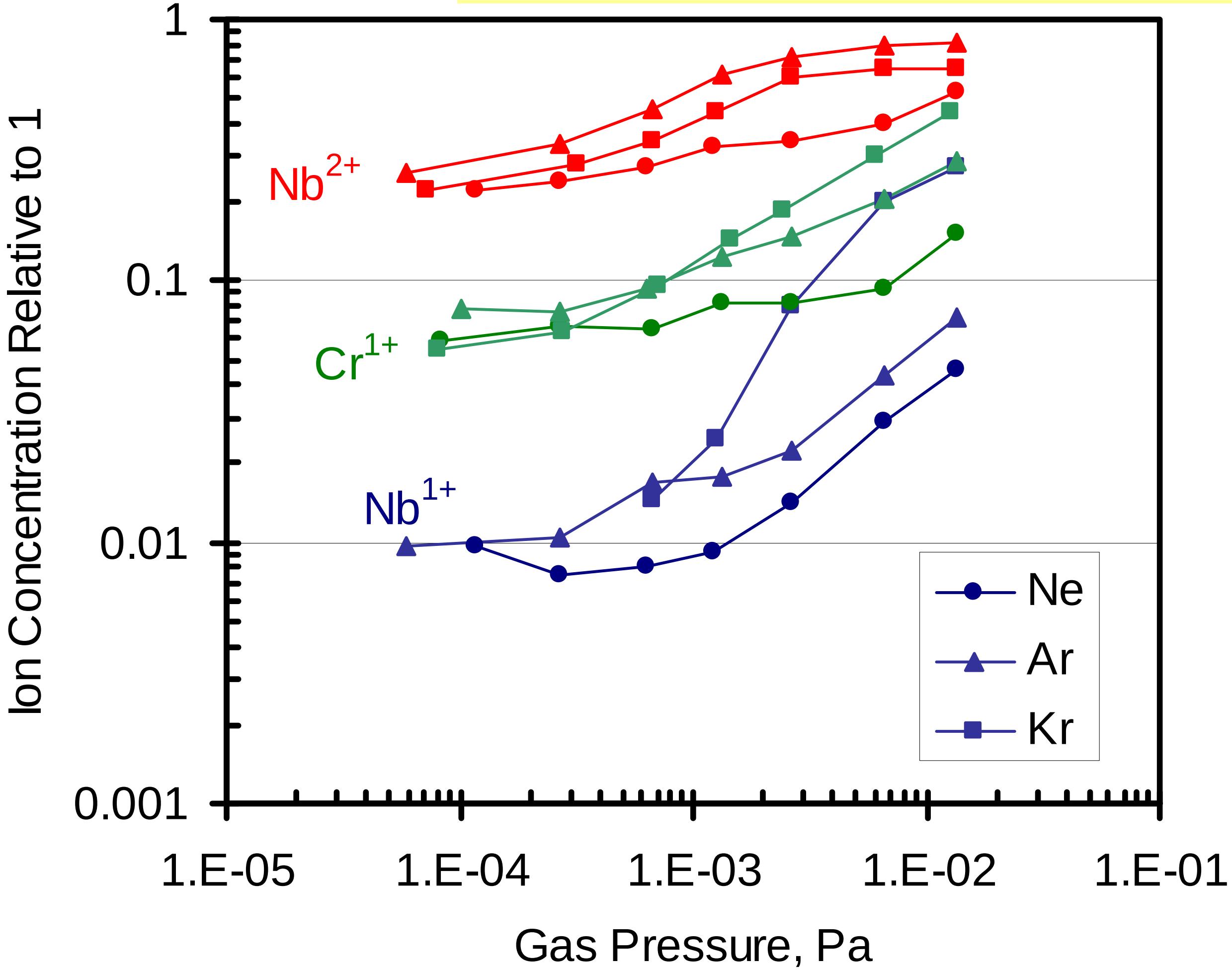
Arutiun P. Ehiasarian, ISDEIV 2002



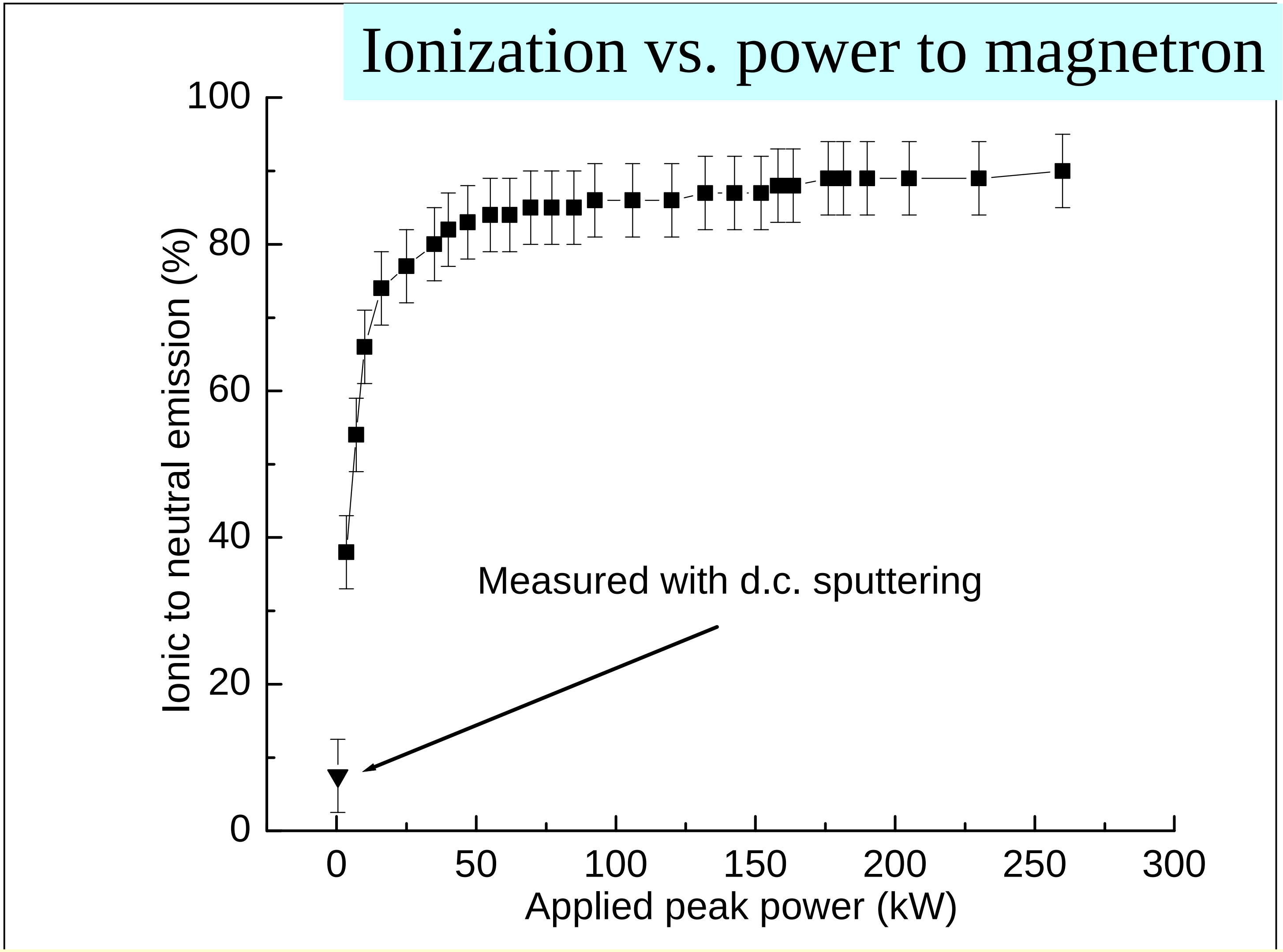
Effect of Noble Gases on Ion Charge States

Metal Ion Charge States < 3+

Arutiun P. Ehiasarian, ISDEIV 2002



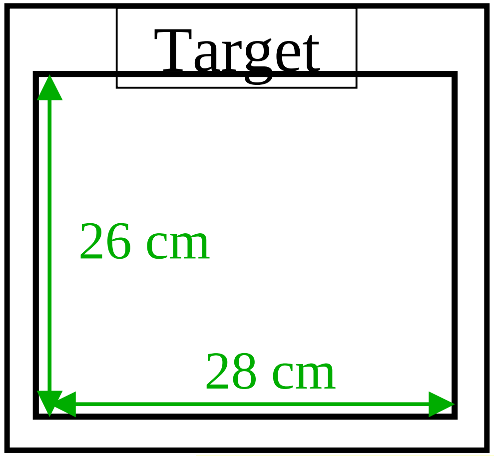
Example of *in-situ* Diagnostics of High Power Pulsed Sputtering

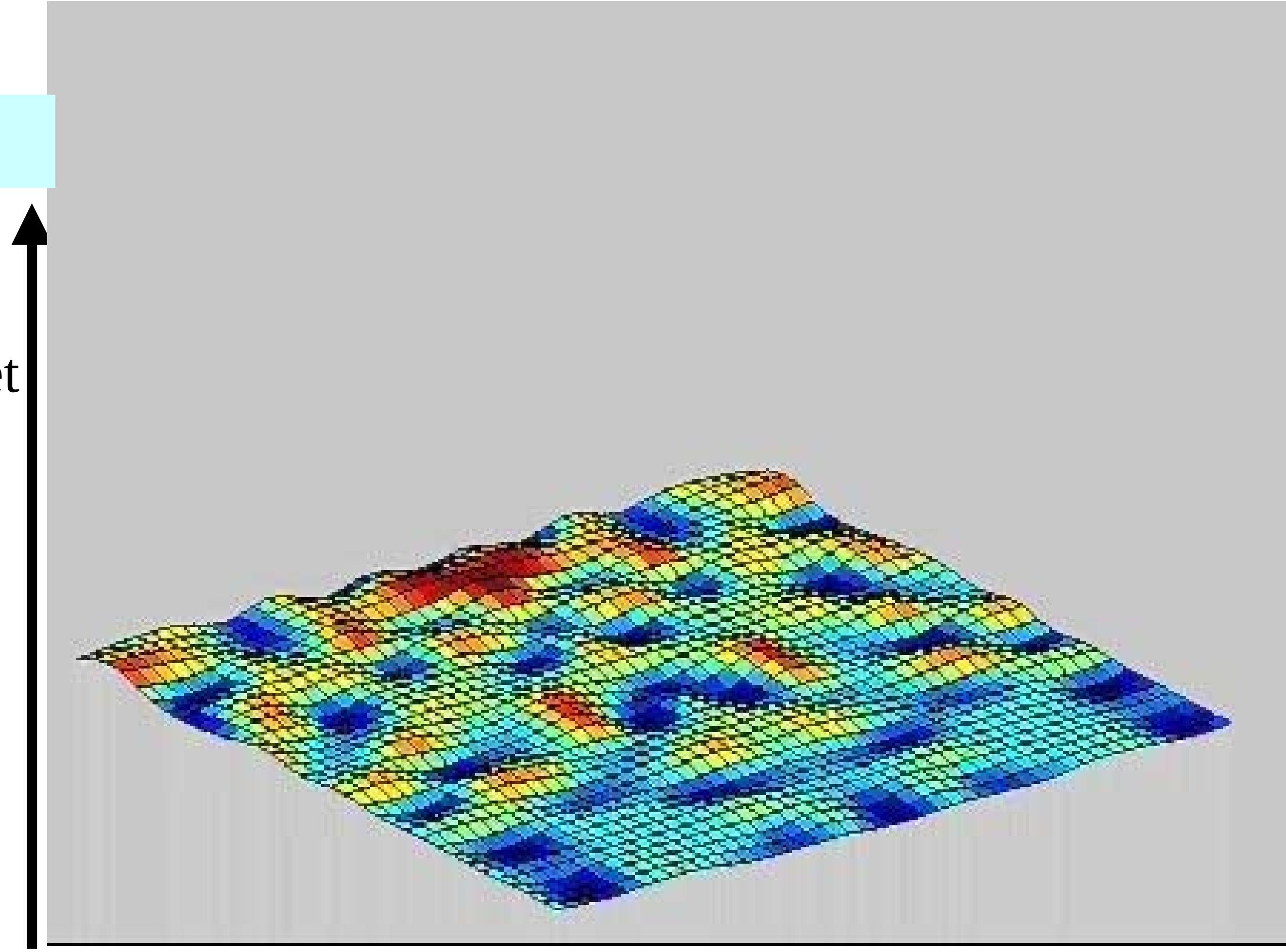


Johan Böhlmark and Ulf Helmersson, Linköping University, Sweden

Example of *in-situ* Diagnostics of High Power Pulsed Sputtering

- (Plasma density)$^{0.33}$
- Time scale: 0-1.8 ms
- 15 cm diameter target



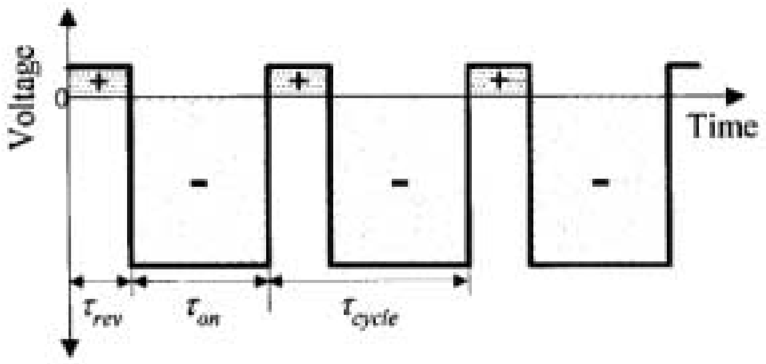


Johan Böhlmark and Ulf Helmersson, Linköping University, Sweden

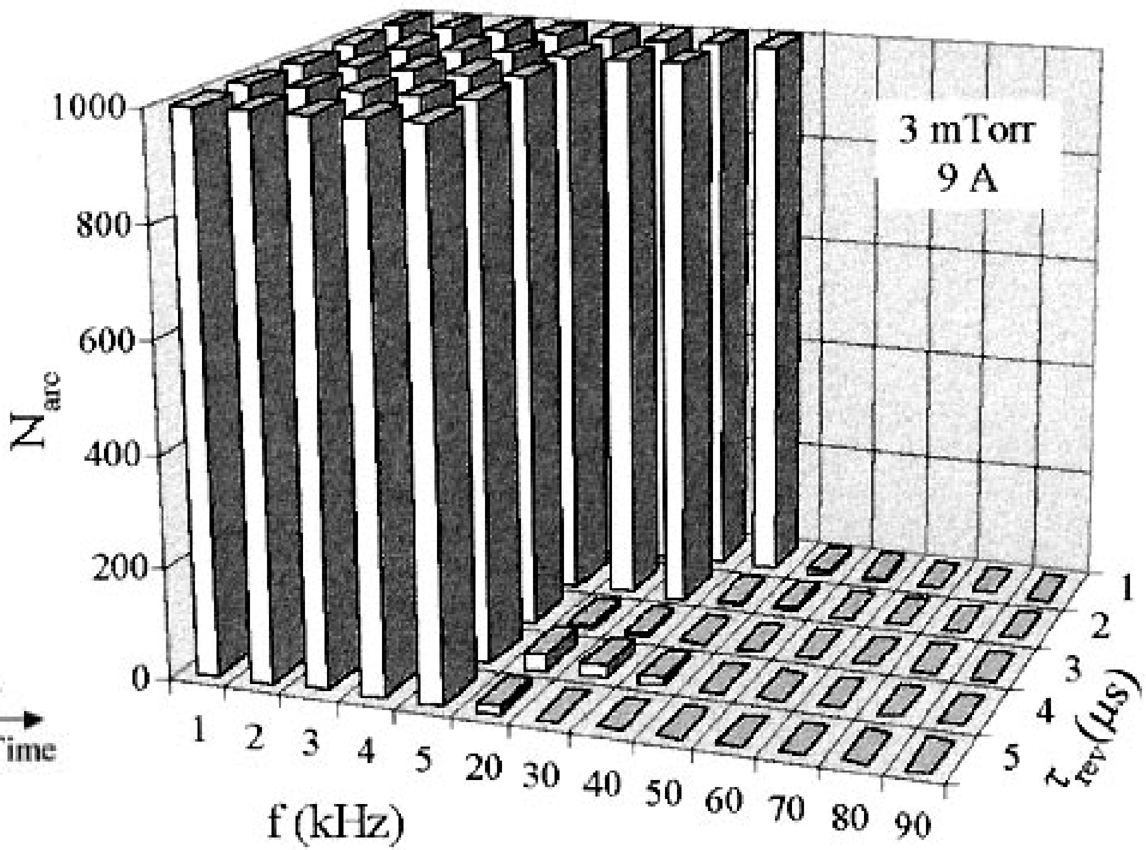
Pulsed Plasma and Arcing

- Example: Al target, Ar/O_2 mixture, bipolar pulsed
- If pulse duration long, or frequency low, arcing occurs

Conditions for explosive electron emission fulfilled



A. Belkind, et al., 41st Annual Tech. Conf. Society of Vacuum Coaters, Boston, 1998.

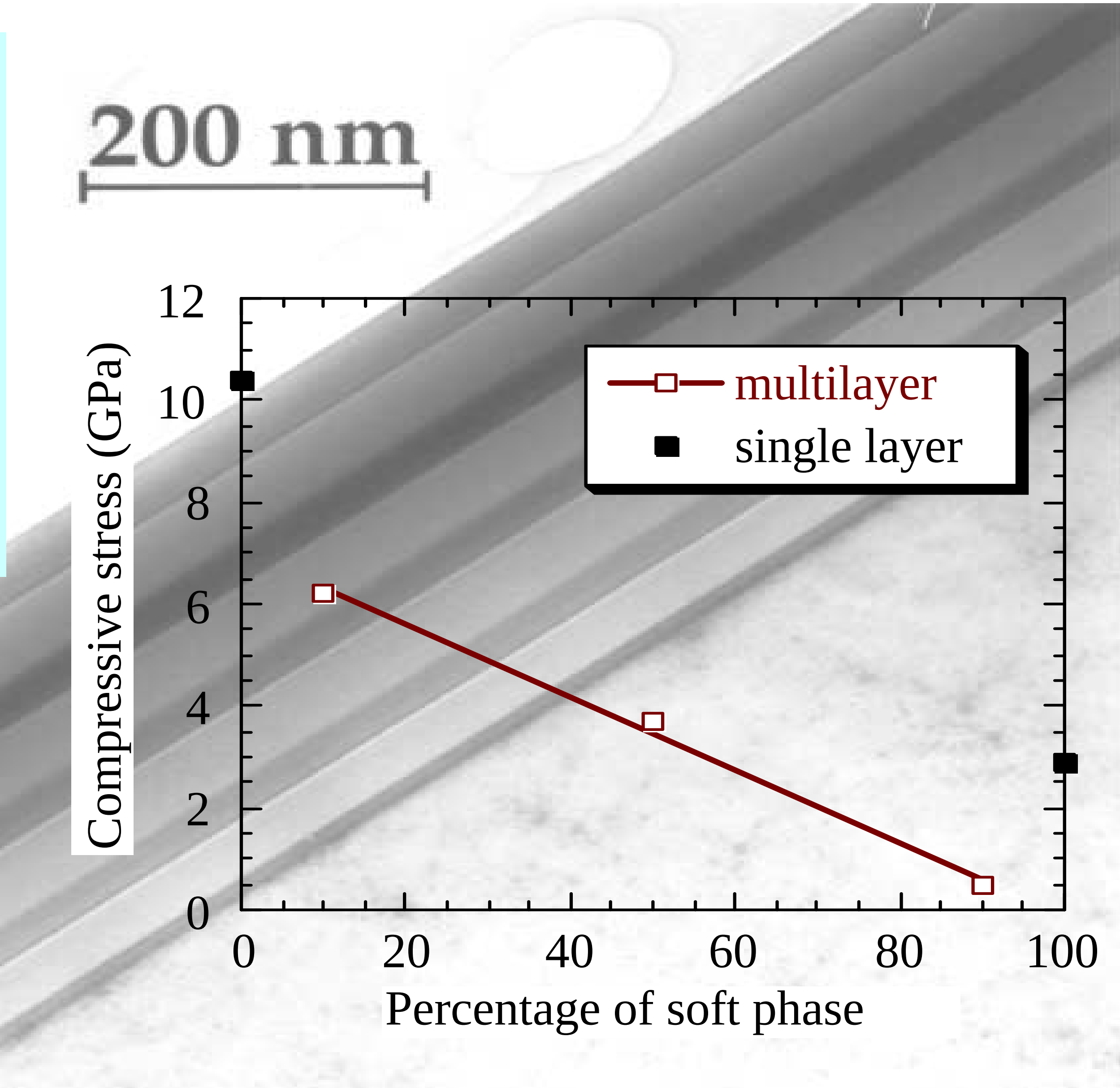


Pulsed Plasma and Arcing

- Arcing:
  - Conditions of explosive electron emission are fulfilled:
  - high electric field (>10^7 V/cm) at target (= cathode) surface due to
    - small sheath thickness at high plasma density
    - surface charging if target is insulating or “poisoned”
  - elevated temperature promotes electron emission and surface atom desorption and evaporation
  - prolonged ion bombardment and thermo-field emission leads to formation and explosive destruction of emission centers
  - voltage “breaks down” from ~500 V to < 50 V
- Arcing = unwanted cathodic arc
  - generates non-uniform plasma and macroparticles

a-C multilayer made by carbon PIIID

- Si substrate, PIII intermixed layer (C, 2.2 keV)
- “hard” a-C (2200 eV) & “superhard” a-C (100 eV) (4 double layers)



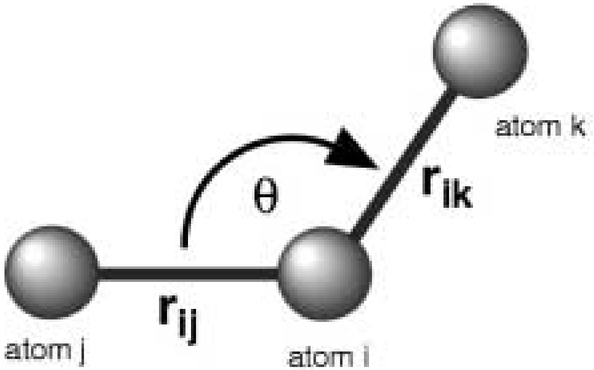
The Environment Dependent Interaction Potential (EDIP)

Courtesy of Dave McKenzie,

- <u>For Silicon</u>: Justo *et al*, *Phys Rev B* **56**, 2539 (1998)
- <u>For Carbon</u>: Marks, *Phys Rev B* **63**, 035401 (2001)

$$U = \sum U_2(r_{ij}, Z_i) + \sum U_3(r_{ij}, r_{ik}, \theta, Z_i)$$

- Interactions vary with the number of neighbours Z_i
- Non spherical terms U_3 are needed to describe sp and sp^2 carbon

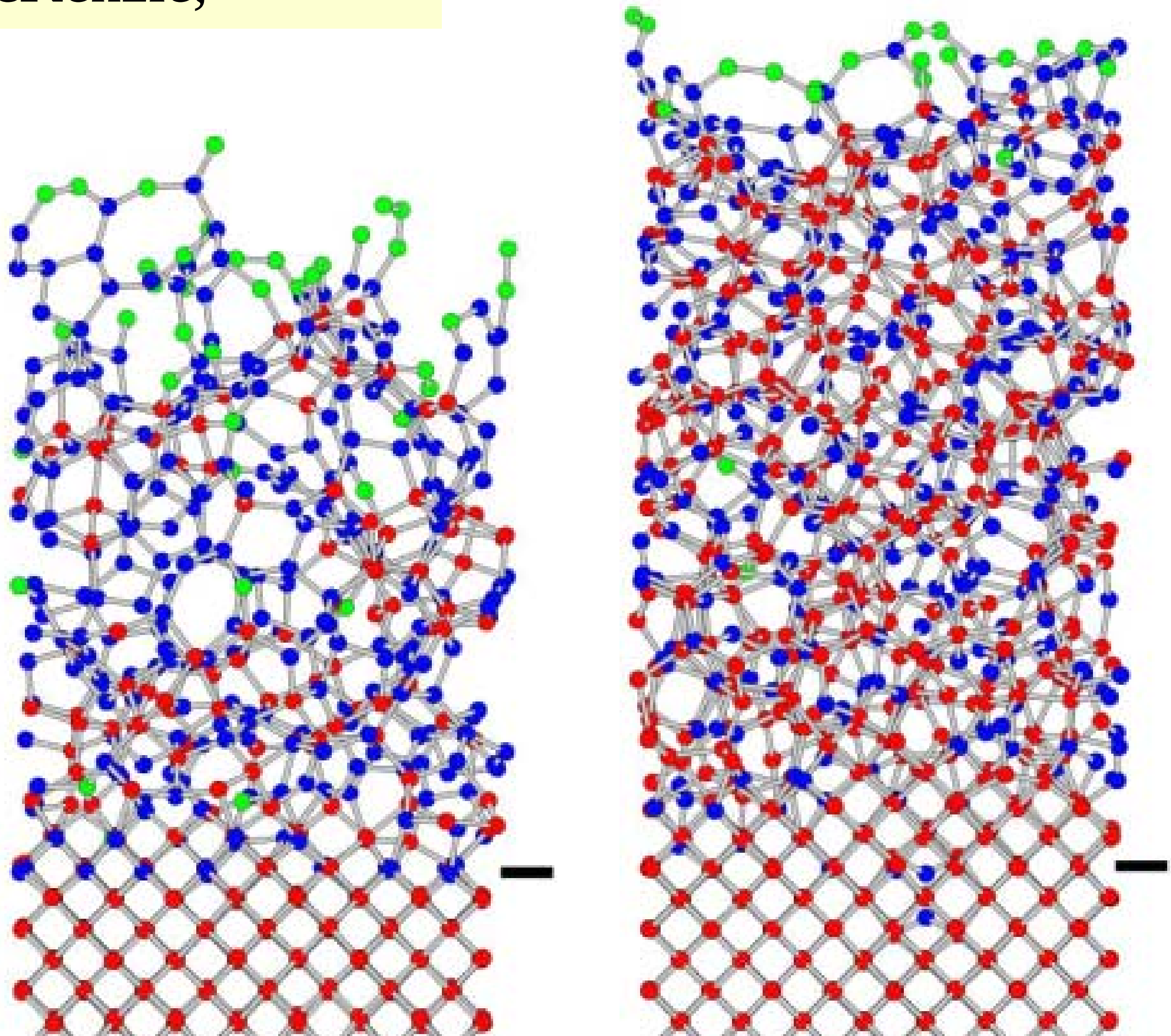


Carbon EDIP Film Growth-Effect of Varying Deposition Energy

Courtesy of Dave McKenzie,

- sp: green
- sp^2: blue
- sp^3: red

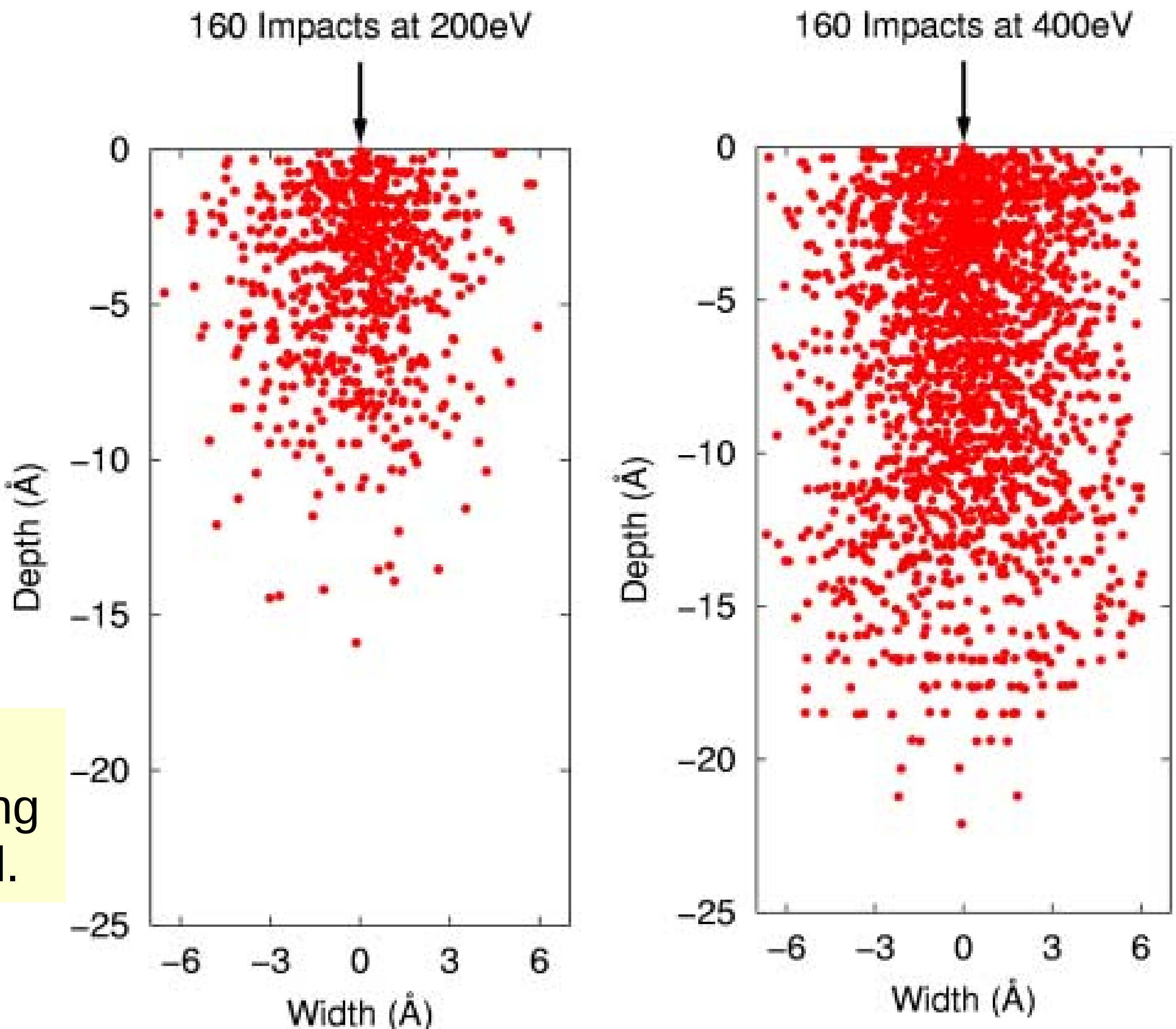
- **Left**: 1 eV
  - mainly sp^2
  - low density
- **Right**: 70 eV
  - mainly sp^3
  - high density



The Shape of a Thermal Spike in Amorphous Carbon

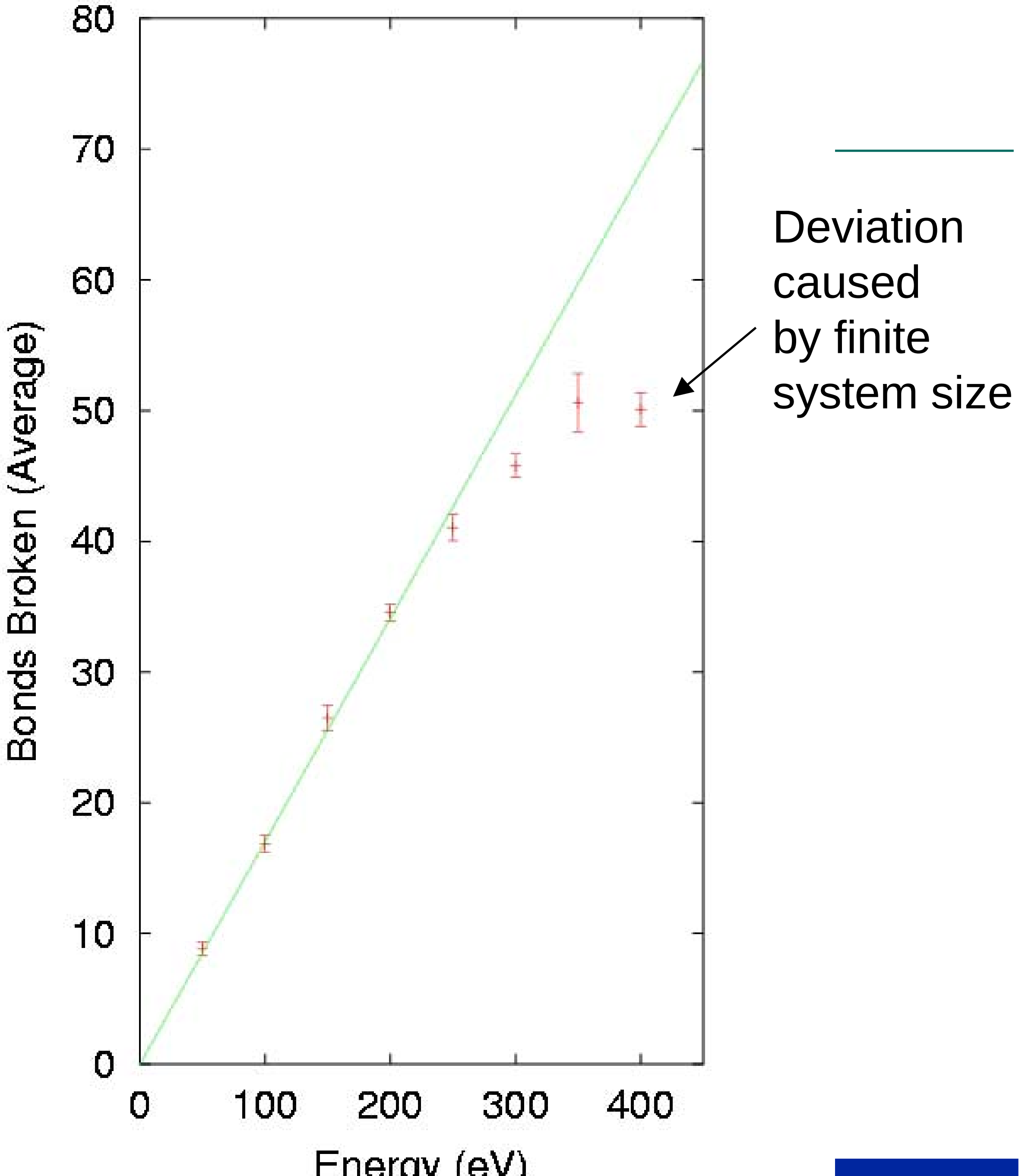
Red=atom moved more than one bond length

Simulations by Gareth Pearce using the EDIP potential.

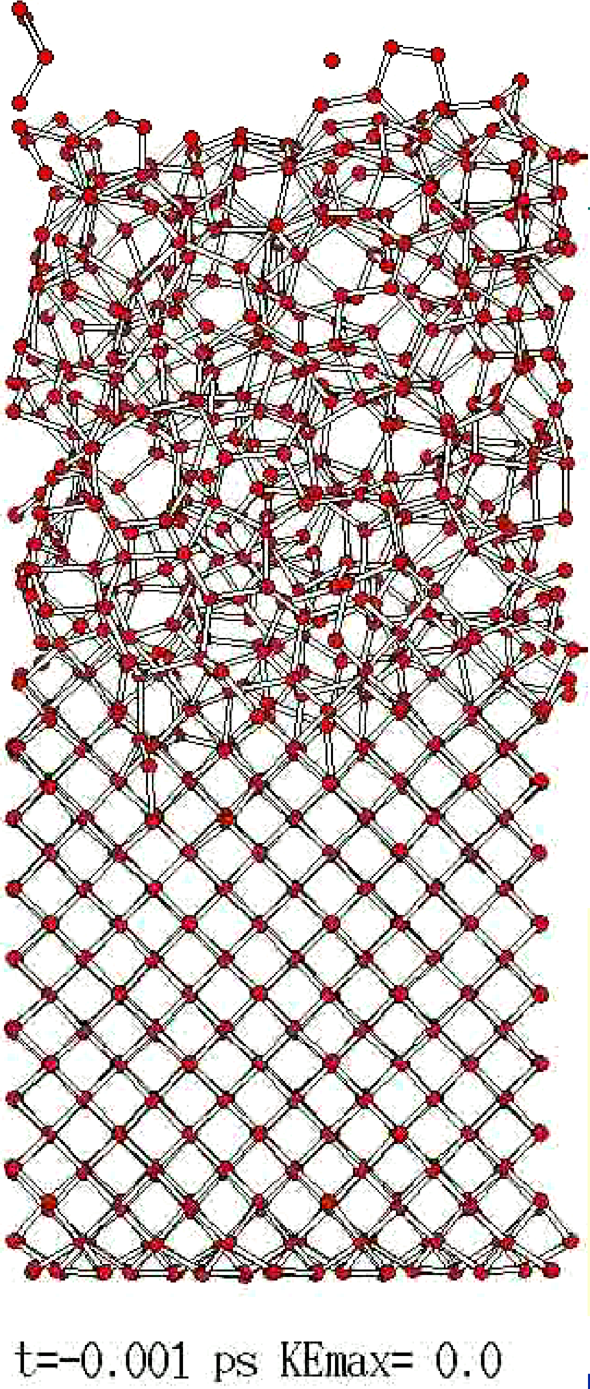


Size of Thermal Spike versus Energy

(average per one ion impact)



Simulations by Gareth Pearce using the EDIP potential.



MD Simulation of Thermal Spike

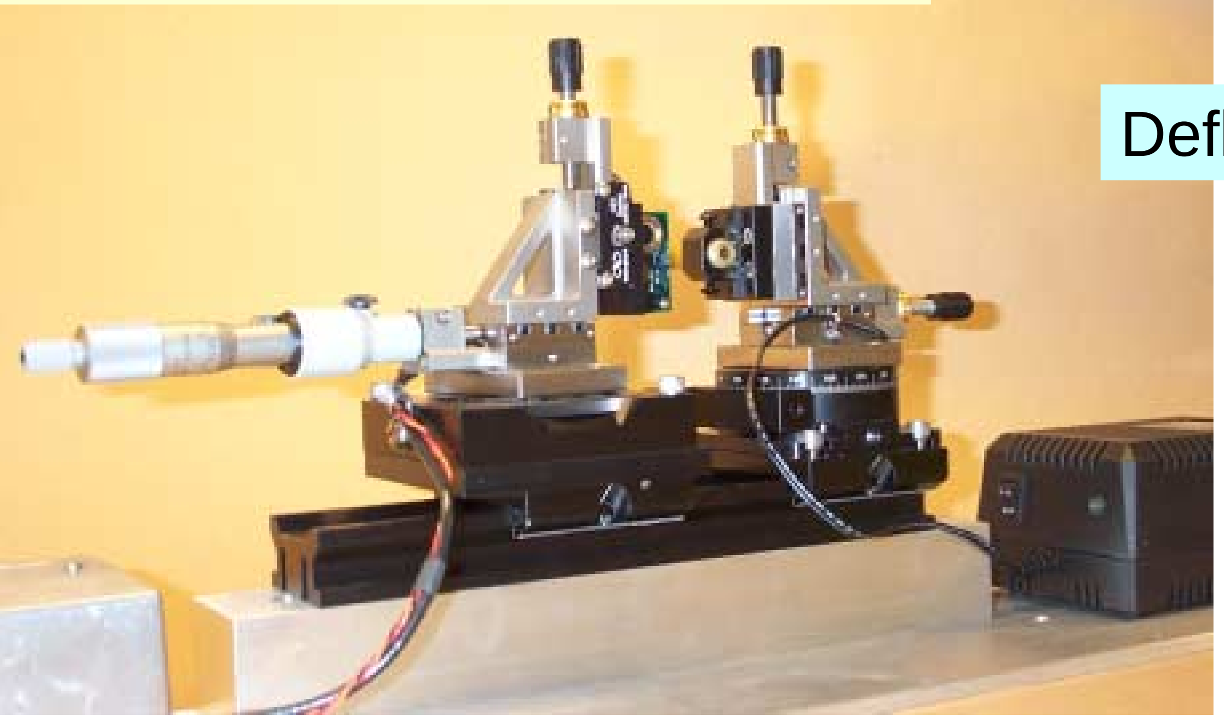
- Movie showing a single 500 eV impact onto a carbon film under stress.
- The average number of atoms affected is about 20.
- Blue atoms received >0.4 eV
- Time scale changes in presentation

Acknowledgements:
Nigel Marks, Jenny Bell, Dave McKenzie.
Movie by Gareth Pearce.

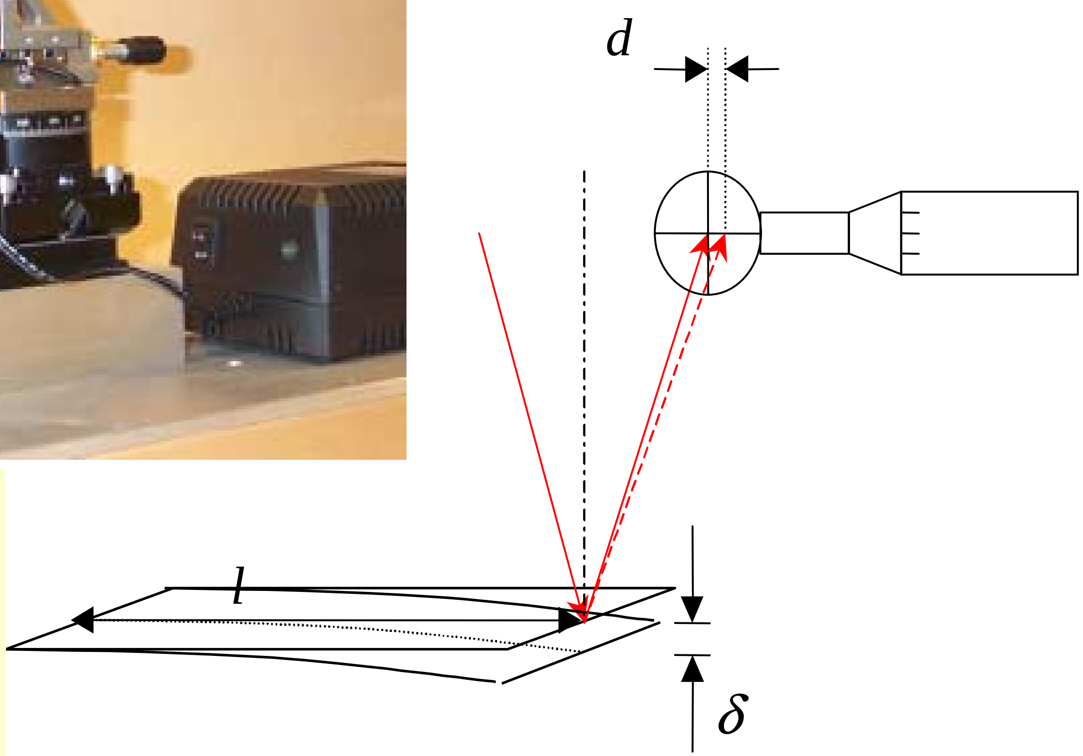
M. Bilek, et al., *IEEE Trans. Plasma Sci.* **31** (2003) 939

In-situ Monitoring of Stress for Stress Control during Growth

Courtesy of O. Monteiro,



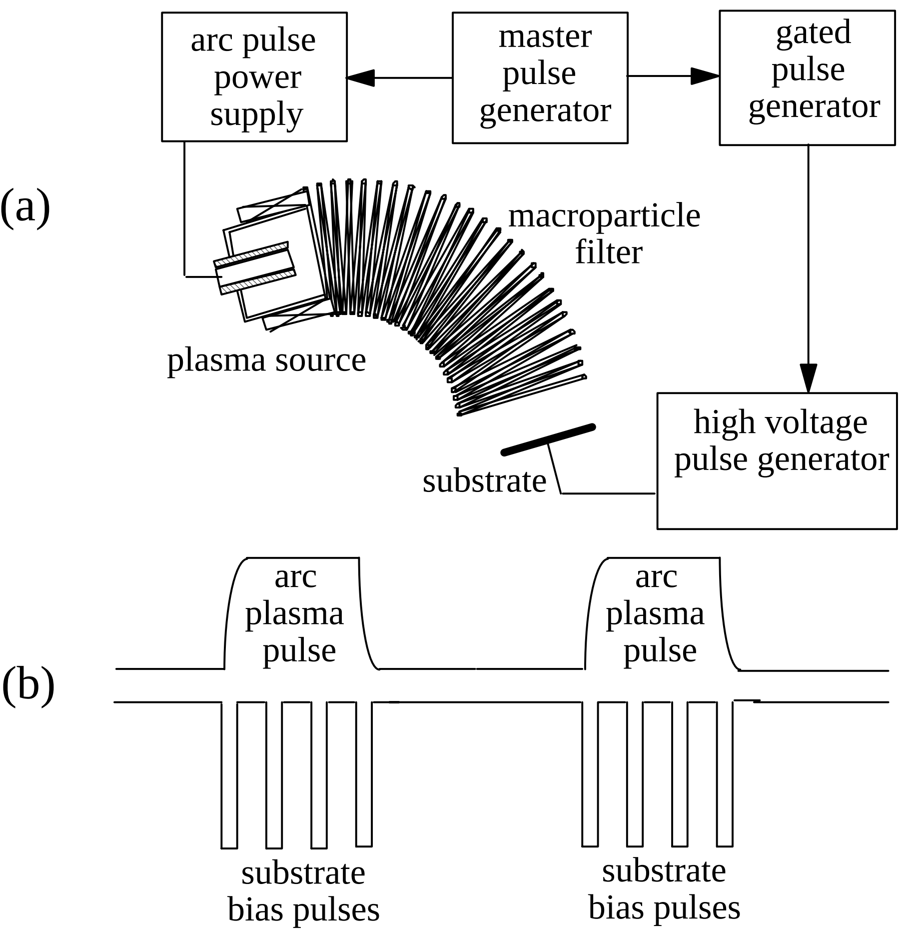
Deflection of a laser beam



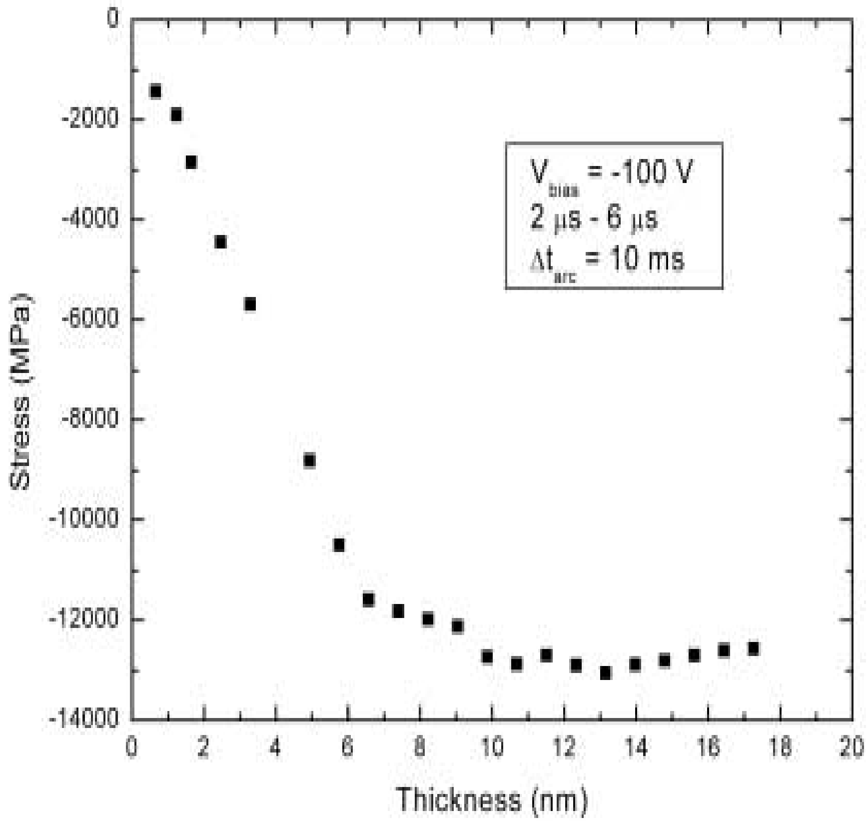
• N. Honda et al., *Sensors and Actuators A* **62**, 663 (1997)
• C Fitz et al. *Surf. Coat. Technol.* **128**, 474(2000)
• G. Moulard et al. *J. Vac. Sci. Technol.* **16**, 736(1998)

Intrinsic Stress in ta-C Films

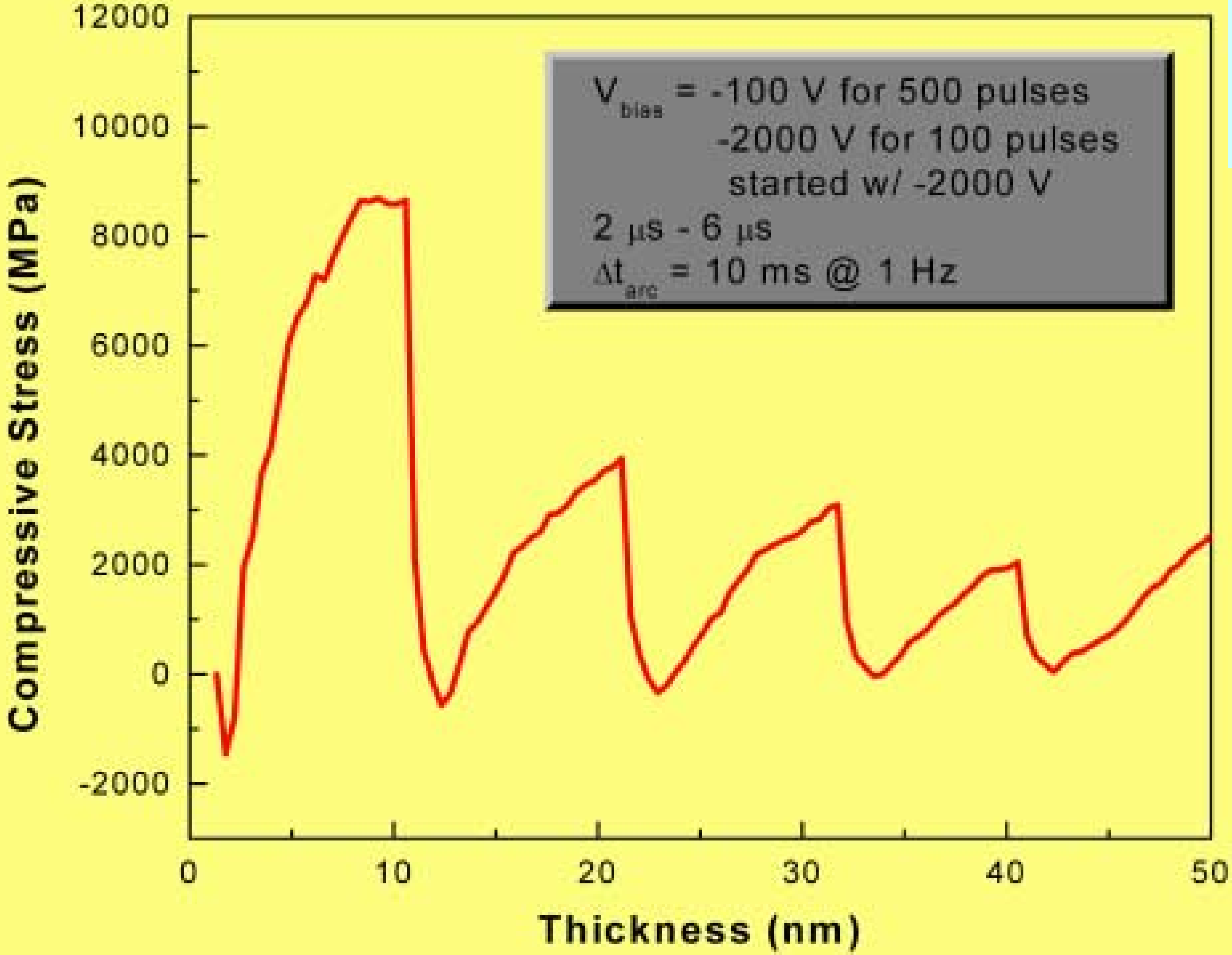
MePIIID, filtered cathodic arc



Bias voltage is used to change carbon energy and therefore bonding and stress in film



Stress Relaxation by Ion Bombardment



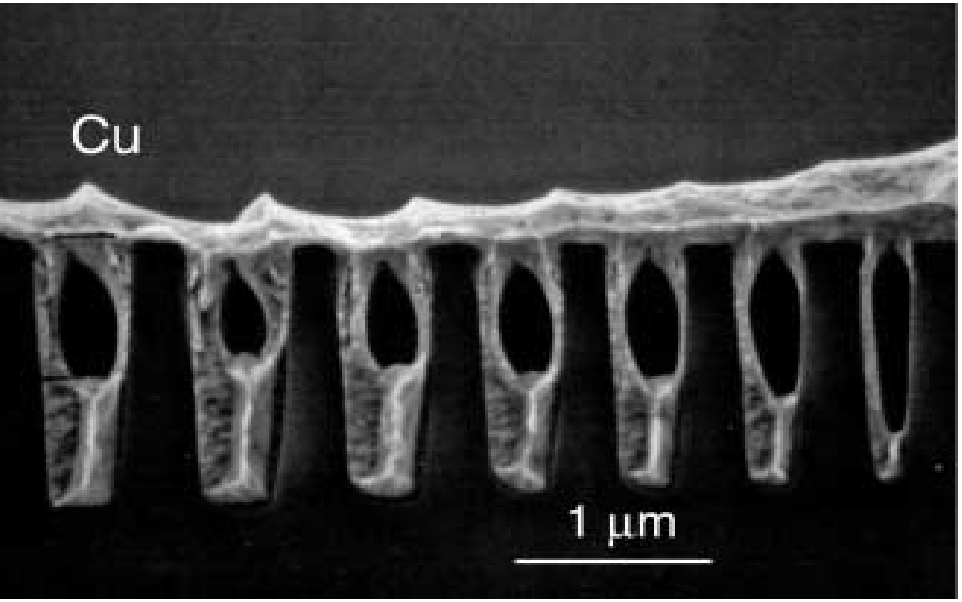
Stress is relaxed by periodically increasing the incident C+ ion energy

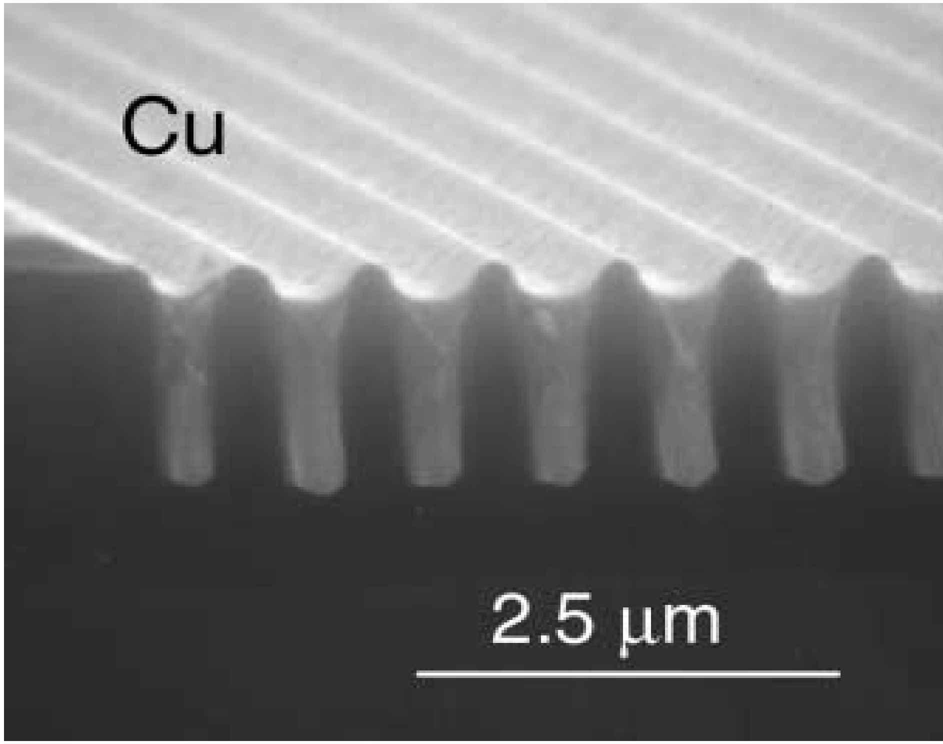
- *Film density is a good indication of sp^3 content.*
- *Density of a monolithic film (V_{bias} = -100 V) = 2.81 g cm^{-3},*
- *Density of relaxed ta-C film = 2.79 g cm^{-3}*
- *Thick ta-C films can be made without thermal annealing*

M. P. Delplanck-Ogletree and O. R. Monteiro, *Diamond & Rel. Mat.*, 2003

Example: Using ionized metal

Copper Metallization of sub-μm trenches





Issue:
voids form if vapor / plasma does not have correct impact angle and energy

perfect filling of trenches using **i-PVD**, but here with **cathodic arc MePIIID**

O.R. Monteiro, *J. Vac. Sci. Technol.* B **17** (1999) 1094

Summary

- Filtered cathodic arcs and pulsed sputtering can be used for energetic condensation of films
- films are dense, often with compressive stress, tunable by bias
- important issues include
  - complete filtering of macroparticle for cathodic arcs
  - complete elimination of arcing (hence macroparticles) for pulsed sputtering
- self-sputtering mechanism may play an important role in pulsed sputtering
- arcing is nothing else than unwanted cathodic arcs
- films with superior properties have been made with both techniques
- Outlook: growing role of in-situ monitoring, stress control